SYNTHESIS OF HEXANITROSTILBENE

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HAMZA TURHAN

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SYNTHESIS OF HEXANITROSTILBENE

Submitted by **HAMZA TURHAN** in partial fulfillment of the requirements for the degree of **Master of Science in Chemistry Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences** _________________

Prof. Dr. İlker Özkan
Head of Department, **Chemistry** _________________

Prof. Dr. B.Lemi Türker
Supervisor, **Chemistry Dept., METU** _________________

Examining Committee Members:

Prof. Dr. Cihangir Tanyeli _____________________
Chemistry Dept., METU

Prof. Dr. B. Lemi Türker _____________________
Chemistry Dept., METU

Prof. Dr. Özdemir Doğan
Chemistry Dept., METU _____________________

Assoc.Prof. Dr.Yahya Suyadal
Chemical Engineering Dept., Ankara University _____________________

Assist. Prof. Dr. Okan Esentürk
Chemistry Dept., METU _____________________

Date:

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Hamza Turhan

Signature :

ABSTRACT

SYNTHESIS OF HEXANITROSTILBENE

Turhan, Hamza
M. S., Department of Chemistry
Supervisor: Prof. Dr. B.Lemi Türker

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HNS (2,2,4,4,6,6-hexanitrostilbene), is an insensitive explosive used by modern armies. It is remarkably stable to heat, shock and stroke. HNS could be used alone as well as together with order explosive materials to improve the performans profiles. Due to its strategic military importance, very many critical points in its synthesis still remain unknown or obscure to scientific publicity. In this project, the synthesis of HNS has been achieved by means of Shipp and TNT/benzoate process. As mentioned above, these processes include various vogue steps which was needed to be enlightened. The Shipp process like the second one is based on TNT as starting material which is produced by the MKEK

Keywords: Thermally stable explosive, Hexanitrostilbene, Trinitrotoluene, Shipp process

ÖZ

HEKZANİTROSİTİLBEN SENTEZİ

Turhan, Hamza
Yüksek Lisans, Kimya Bölümü
Tez Yöneticisi: Prof. Dr. B.Lemi Türker

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HNS (2,2,4,4,6,6)hexanitrostilbene), modern ordular tarafından kullanılan duyarsız bir patlayıcıdır. HNS hayret verici bir şekilde ısı, şok ve darbeye karşı dayanıklıdır. HNS tek başına patlayıcı olarak kullanılabildiği gibi diğer bazı patlayıcılarla performansı artırmak maksadıyla mürekkep bir tarzda da kullanılmaktadır. HNS sentezinin bir çok noktası, maddenin stratejik askeri öneminden dolayı bilimsel çevrelerde ya bilinmemekte ya da belirsiz kalmaktadır. Bu proje çerçevesinde HNS sentezi, Shipp ve TNT/benzoate yöntemleri uzerinden gerçekleştirilmeğe çalışılmıştır. Yukarıda bahsedildiği üzere bu yöntemlerin aydınlatılması gereken bir çok basamağı vardır. Shipp yöntemi ikincisinde olduğu gibi, MKEK tarafından üretilen TNT'ye dayanmaktadır.

Anahtar kelimeler: Isıya dayanıklı patlayıcı, Hekzanitrostilben, Trinitrotoluen, Shipp yöntemi

To My Family,

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INTRODUCTION

1.1. EXPLOSIVES

Compounds that contain polynitro groups are always highly energetic [1]. They can provide a large amount of energy and heat after they are burnt and are employed extensively as the main ingredient in explosives and propellants. Some well-known explosives such as TNT (2,4,6-trinitrotoluene), RDX ,TNAZ,HNS,HNAB and TATB are all energetic polynitro compounds [2]. Normally, a compound having more nitro groups is more energetic, and introducing an oxidative nitro group causes close contact with the energetic parent material and improves the oxygen balance, ensuring favorable performance as an explosive (or propellant).

1.2. CLASSIFICATION OF EXPLOSIVES

Classification of explosive materials is based on various criteria. They may be classified both from the chemical point of view and according to their uses. From the chemical viewpoint, explosives can be distinguished as individual chemical explosives and mixtures. The main subclasses of the former are divided into (Figure 1.1) nitro compounds, 2) nitric esters, 3) nitramines, 4) derivatives of chloric and perchloric acids, 5) azides, 6) various compounds capable of producing an explosion, for example fulminates, acetylides, nitrogen rich compounds such as tetrazene, peroxides and ozonides, etc.

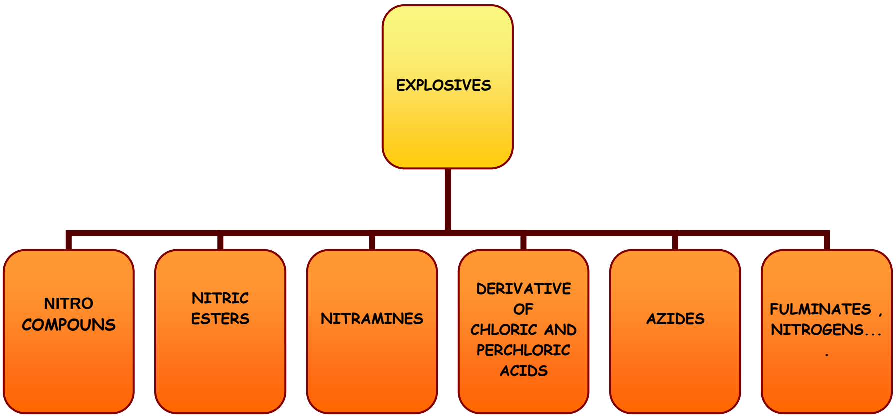


Figure 1.1. Some groups of explosives.

Individual substances are explosive if their molecules contain groups which confer upon them explosive properties. The first attempt at a systematic approach to the relation between the explosive properties of a molecule and its structure was made by van't Hoff [3]. He pointed out, that the explosive molecules generally contain the following groups.

1) O-O linkage in peroxides, ozone and ozonides,
2) O-Cl in chlorides and perchlorates,
3) N-Cl in nitrogen chloride,
4) N=O in nitro compounds, nitric acid esters and salts,
5) N=N in diazo compounds, hydrazoic acid, its salts and esters,
6) N=C in fulminates and cyanogen,
7) C≡C in acetylene and acetylides.

A further effort to establish a relationship between explosive properties and structure was made by Pletz [4]. He proposed the theory of "explosophores" and "auxoploses" in a way analogous to Witt's suggestion of chromophores and auxochromes in the dyes, and Ehrlich's toxophores and autotoxes in chemotherapeutics.

According to Pletz the explosive properties of any substance depend upon the presence of definite structural groupings, called explosophores. The auxoploses fortify or modify the explosive properties conferred by the explosophore. Pletz divided all explosives into eight classes containing the following groups as explosophores:

(1) $–NO_2$ and $–ONO_2$ in both organic and inorganic substances
(2) –N=N- and -N=N=N- in inorganic and organic azides
(3) –N=C in fulminates
(4) $–NX_2$, for example in NCl_3 (X: a halogen)
(5) –O-O- and –O-O-O- in inorganic and organic peroxides and ozonides, respectively
(6) $–OClO_2$ and $–OClO_3$ in inorganic and organic chlorates and perchlorates, respectively
(7) -C≡C- in acetylene and metal acetylides
(8) M-C metal bonded with carbon in some organometallic compounds.

Although this classification is in principle correct, the distinction between the terms "explosophore" and "auxoplose" is very vague and of little practical value. A further step in the classification of explosives was made by Lothrop and Handrick [5], who collected and classified all the available information on the performance of explosives and related it to four factors. Those are the oxygen balance, "plosophoric" groups, "auxoplosive" groups and heat of explosion.

A plosophore has been defined as a group of atoms which is capable of forming an explosive compound on introduction into a hydrocarbon. According to these authors there exist two classes of plosophores differing sharply in effectiveness and consistency in producing power. Hence, it is suggested that these be called “primary” and “secondary” plosophores. Primary plosophores include aromatic and aliphatic nitro groups, nitrate esters, and the nitramine group. The secondary plosophores include groups such as azo, azide, nitroso, peroxide, ozonide, perchlorate, etc. If more than one type of these groups is present, such a molecule may be named a hybrid according to Lothrop and Handrick [5].

Groups which do not themselves produce explosive properties, but may influence them (in the same way that auxochromic groups vary the color intensity and shade of a dye), are called auxoplosives by these authors. As examples of such groups, we may quote hydroxyl, carboxyl, chlorine, sulfur, ether, oxygen, amine, etc.

Although the classification of groups existing in explosive molecules suggested by Lothrop and Handrick [5] may generally be accepted, their far-reaching postulations concerning a close relation between the oxygen balance and performance of explosives aroused strong criticism [6], because the oxygen present, for example, in carbonyl or hydroxyl groups, has little effect on the performance of an explosive.

This is due to the high heat of formation of C-O and C-O-H bonds. The low value of the explosive power of oxygen atoms bonded with carbon C≡C bonds has great significance in relation to the performance of explosives. Because of that reason, the performance of picric acid (trinitrophenol) is only very slightly higher than that of and hydrogen atoms in such a group as COOH had already been stressed by Stettbacher [7], who has pointed out that an exception is provided by peroxides and ozonides which form exothermic bond that considerably enhance explosive performance.

However, the slightly better performance of picric acid compared with trinitrobenzene is probably the result of the former’s greater ability to detonate. The ease of detonation of picric and styphnic acids as compared with trinitrobenzene is well known. Smolenski and Czuba pointed out that dinitrophenol detonate more readily than dinitrobenzene [8]. From the classic work of Wöhler and Wenzelberg, it is also well known that the sensitivity to impact of aromatic nitro compounds increases with increase in the number of substituents for a given member of the nitro groups [9].

According to their uses explosives are divided into i) primary explosives or initiators ii) high explosives, and iii) propellants (low explosives). Primary explosives and their mixtures are divided into those used for filling ignition caps and those used in detonators [10]. High explosives may be classified according to their physical properties as powdery, meltable, semi-meltable and plastic. On the other hand, propellants may be grouped on the basis of chemical composition into gun powder and similar mixtures, nitrocellulose and nitroglycerine powders. With respect to their uses and some properties they are divided into black powder, smokeless and flashless powders, and rocket propellants. Mercury azide and lead styphnate (Figure.1.2.) are common primary explosives used in military applications [11].

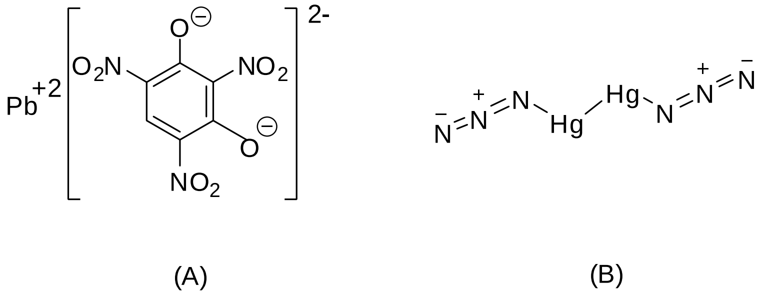
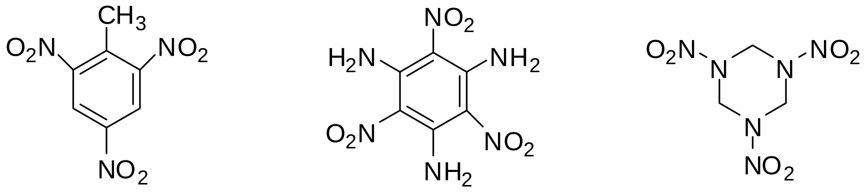

(A) (B)

Figure 1.2. (A): Lead Styphnate, (B): Mercury Azide.

Secondary explosives also known as high explosives could not easily detonated by the shock impact or friction. The sensitivity of secondary explosives is much more lower than primary explosives [12]. Commonly, secondary explosives initiated by the help of primary explosives [13]. Secondary explosives are so stable that some of them cannot be detonated even in fire. Some examples of secondary explosives are TNT, TATB, and RDX (Figure 1.3).



(A) (B) (C)

Figure 1.3. (A): TNT, (B): TATB, (C): RDX.

1.3. CHEMICAL NATURE OF EXPLOSIVES

The properties discussed for explosives include the followings:

1.3.1. Heat of Fusion

The heat of fusion is the amount of heat necessary to transform (melt or fuse) a unit of solid into a liquid at the same temperature and standard pressure. This quantity is usually expressed in terms of calories per gram [14].

1.3.2. Heat of Vaporization

The heat of vaporization is the amount of heat necessary to convert a unit of liquid to vapor at the same temperature. This quantity is usually expressed in terms of calories per gram [15].

1.3.3. Heat of Sublimation

The heat of sublimation is the amount of heat necessary to convert a weight of solid directly into vapor in a constant temperature process. This quantity is usually expressed in calories per gram [16].

1.3.4. Heat of Detonation

Two quantities are usually given for the heat of detonation, one with liquid water in the reaction products and one with gaseous water in the reaction products [17]. The test used to determine these quantities uses a standard calorimeter. When the water is allowed to condense to liquid, the total heat produced by the detonation reaction is measured. The heat of detonation with gaseous water more accurately reflects the process of detonation in a non-laboratory setting [18]. However, the results are less reproducible.

1.3.5. Heat of Combustion

The heat of combustion is the amount of heat produced when a material is burned [19]. This differs from the heat of detonation because the products formed are different. Generally, the products formed in combustion are at a lower energy level than the products formed during detonation. For example, carbon monoxide and carbon dioxide may be products of both detonation and combustion for a particular explosive [20]. However, the detonation process might produce more carbon monoxide, while combustion might produce more carbon dioxide [21].

,

1.3.6. Sensitivity

Various external stimuli can cause release of the energy contained in energetic materials [22]. Knowing the response of individual energetic materials to specific stimuli is important from the point of view of safety and in determining the suitability of a material for a specific application. The response to a blow is called impact sensitivity [23]. Traditionally, explosives have been subjected to falling weights to measure impact sensitivity. The results are then reported as the distance a given weight must fall to produce detonation 50 percent of the time [24]. The physical significance of this type of test has recently been questioned. The results are more qualitative than quantitative.

For example, there is no question that lead azide is much more impact sensitive than TNT and that TNT is much safer to handle than lead azide. But the quantitative meaning of "much more impact sensitive" is ill-defined. The results of this test should be considered for general comparisons among explosive compounds. These same remarks are also valid for sensitivity to friction [25]. Sensitivity of an explosive to shock is a very reproducible quantity. Shocks generated by a donor explosive can cause detonation in another explosive material. The strength of the shock wave required is a relative measure of the sensitivity of the material under test. In practice, a strong shock is produced and attenuated in an inert medium [26]. The width of the medium that will allow detonation in 50 percent of the trials is reported as the test result. These tests are called gap tests [27]. Gap test results are much more reliable data than impact test results, although there is some dependence on the geometry of the test apparatus [28]. Electrostatic sensitivity is an important quantity because of safety. Some explosives can be detonated by the shock of a person charged with static electricity [29]. Thermal sensitivity is an important quantity which needs to be determined in considering explosives for applications. In some cases, such as in the warhead of a high speed intercepting missile, the heat generated during flight can cause detonation of explosive charges that are not highly resistant to heat [30].

1.3.7. Brisance

Brisance is the shattering capability of an explosive [31]. Several tests are commonly used to determine brisance. In the sand test 0.400 grams of the explosive are placed in 200 grams of sand and detonated [31]. The amount of sand crushed by the explosive is a measure of brisance. The plate dent test, in which a sample of the explosive is detonated in close proximity to a metal plate, is also used to measure brisance [32]. The size of the dent is proportional to the brisance. Another method of measurement involves detonating a sample of explosive on top of a cylinder made of lead and measuring the contraction in length of the cylinder [33]. The number, size distribution, and velocity of fragments produced by an explosive in a projectile is also related to the brisance of the explosive [33].

1.3.8. Detonation Velocity

The detonation velocity is simply the rate at which the detonation reaction proceeds through an explosive [34]. This quantity is closely related to the brisance. With a limited number of exceptions, increased detonation velocity increases brisance [34].

1.3.9. Power

The power of an explosive is the total energy available to do work [35]. This is a different quantity than brisance, even though on the surface they appear rather similar. Consider two explosives, ammonium nitrate and RDX. If a charge of each is placed beneath a boulder, the ammonium nitrate might hurl the boulder many meters but the RDX might pulverize the boulder into many fragments [36]. The former quality is power whereas the latter quality is brisance. Power is measured by the Trauzl lead block test in which a sample of the explosive is detonated in a cavity in a lead block [37]. The expansion of the cavity is a measure of the power of the explosive. The ballistic pendulum and ballistic mortar tests are also used to measure power. A heavy weight is accelerated by the detonation of an explosive. The swing of the pendulum or movement of the mortar's weight is a measure of the power of the explosive [37]. The oxygen balance of the explosive is closely related to the power. The oxygen balance is the ratio of oxygen contained in the explosive material to the amount of oxygen required for complete oxidation of the explosive material [38]. Explosive compositions with better oxygen balances are more powerful.

1.3.10. Stability

Stability is the ability of energetic materials to retain, unaltered, such properties as detonation velocity and sensitivity after long periods of storage under adverse conditions [39]. All energetic materials are unstable to some extent. The degree of instability varies greatly. TNT can be stored for 20 years with no change in stability while other explosives, which are not used by the military or commercially, decompose and/or detoriate in a matter of days or minutes [40].

1.4. POLYNITRO ARYLENES AS EXPLOSIVES

Polynitro arylenes are the important class of high energy materials. They hold central position in the field of military explosives. Trinitrotoluene (TNT) was the most commonly used polynitro benzene derivative in military applications [41]. It was first synthesized in 1863 by the nitration of toluene by sulfuric acid and nitric acid mixture [41] (Figure 1.4). TNT is classified as a secondary explosive because it is less susceptible to initiation and requires a primary or initiating explosive to ignite it. TNT can be used as a booster or as a bursting charge for high-explosive shells and bombs.

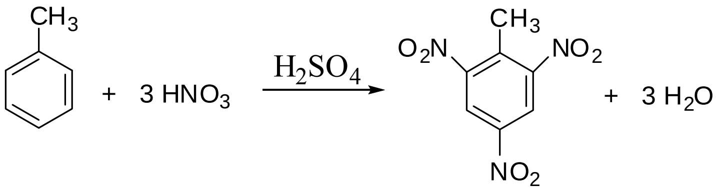


Figure 1.4. The synthesis of TNT.

The advantages of TNT include low cost, safety in handling, fairly high explosive power, good chemical and thermal stability, compatibility with other explosives, a low melting point favorable for melt casting operations and moderate toxicity [42]. TNT is still used effectively as an energetic binder for cast compositions.The cyclotols (RDX/TNT), Torpex (RDX/TNT/A1), pentolite (PETN/TNT) and PTX-1 (RDX/tetryl/TNT) are all secondary explosive compositions based on TNT.

Many highly nitrated polynitroarylenes like TNT invented during the last century [43]. Although these are powerfull explosives lots of them are not practical explosives because of their poor chemical stability.

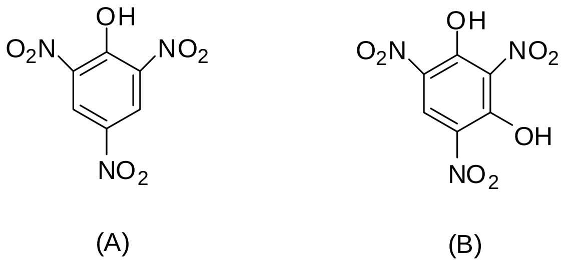


Figure 1.5. (A): 2, 4, 6 - Trinitrophenol, (B): 2, 4, 6 - Trinitroresorcinol.

For example 2, 4, 6 - Trinitrophenol (Figure 1.5), commonly known as picric acid, was once used as a military explosives; however, its highly acidic nature enables metals to corrode readily [44]. These kinds of reaction lead to many accidents because of the high sensitivity of metal picrate. 2, 4, 6 - Trinitroresorcinol (Figure 1.5) is another unstable polynitro aromatics. Because of its acidic property is highly dangerous. The acidity of polynitroaromatics comes from inductive effect of nitro compunds [45]. Having benzene four or more nitro groups at the meta positions and its substituted derivatives are all chemically unstable [46]. Scientists work for thermally stable polynitroarylenes with a low sensitivity to impact and friction.

During the last century, lots of stable polynitroarylenes have been invented [47]. Most famous ones are TATB, DIPSO, HEXYL, HNAB and HNS.

TATB is a thermally stable and remarkable explosive with many stable characteristics including shock, percussion, and friction insensitivity. It is usable in the 260-290 °C range. Such properties come from strong intermolecular and intramolecular hydrogen bondings between the adjacent nitro and amino groups [48]. TATB used in modern military technologies especially of ground misiles, air to air misiles and ground to air missiles. In recent years, it is the preferred conventional secondary high explosive in nuclear weapons [49]. The current industrial method to synthisize TATB is nitration of trichlorobenzene to give 2, 4, 6 - trichloro trinitrobenzene with sulfuric acid and nitric acid mixture, then amination with ammonia in toluene medium gives TATB (Figure 1.6) [50].

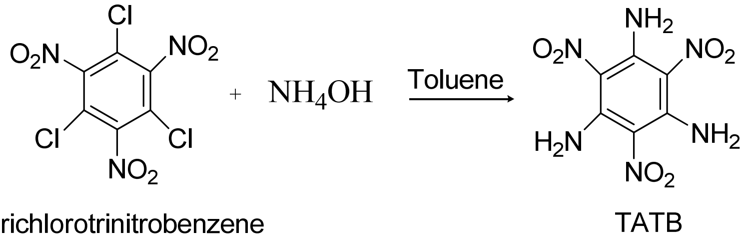


Figure 1.6. The synthesis of TATB.

Alternatively TATB synthesized with starting nitration of 1, 3, 5 - trihydroxybenzene then alkylation of resulting substance and finally amination gives 81 % TATB. Bellamy suggests some modification in this process (Figure 1.7) [51].

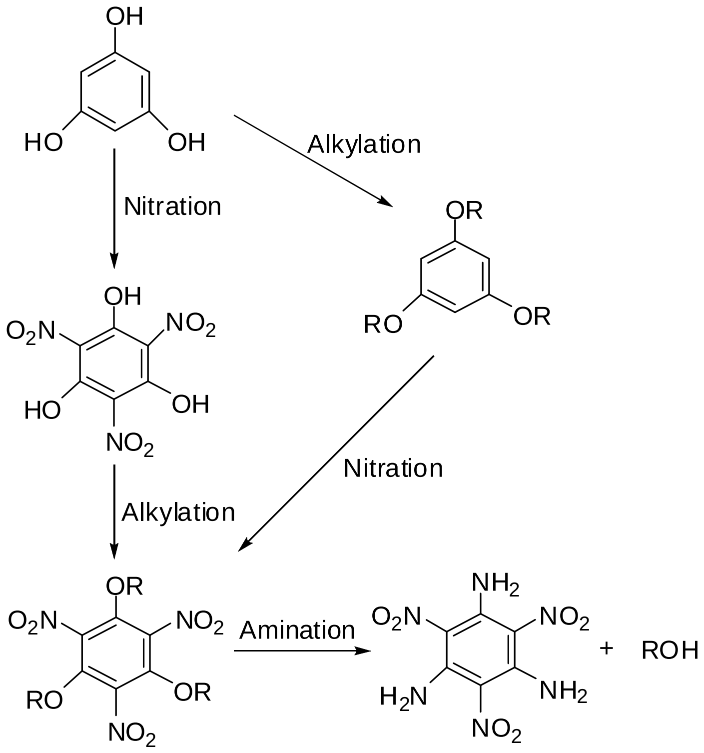


Figure 1.7. The sythesis of TATB from trihydroxybenzene.

A similar synthesis method used by researchers at Pantex, Amarillo, Texas, to reduce chlorine contamination (Figure 1.8) [52]. Although high yield is obtained, the applicability of this procedure in large scale involves some problems.

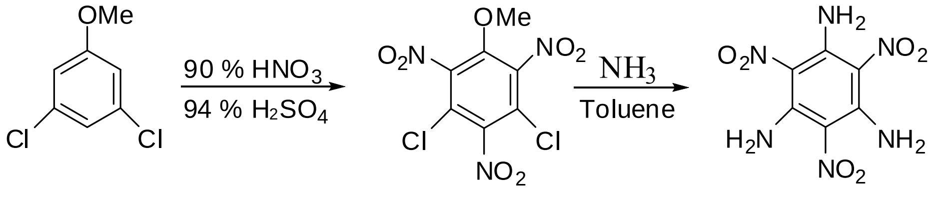


Figure 1.8. The synthesis of TATB with reducing chlorine content.

Another important thermally stable explosive is 2,4,6 - trinitrobenzene (PCS; 2,2',4, 4',6,6' - hexanitrodiphenyl sulfone (DIPSO)). It was synthesized by oxidation with CrO_3 as oxidant in HNO_3 medium of a intermediate, 2,2’,4,4’,6,6’-hexanitrodiphenyl sulfone (DPS), which was prepared by condensation reaction using 2, 4, 6 - trinitrochlorobenzene and sodium thiosulfate as the starting materials (Figure 1.9) [53]. Differential scanning calorimetry (DSC) exothermic peak shows that it melts and decomposes at 360.1 °C. It used in oil explosives and JF1 (20 % TNT, 30 % RDX, 50 % DIPSO) is prepared based on DIPSO [54].

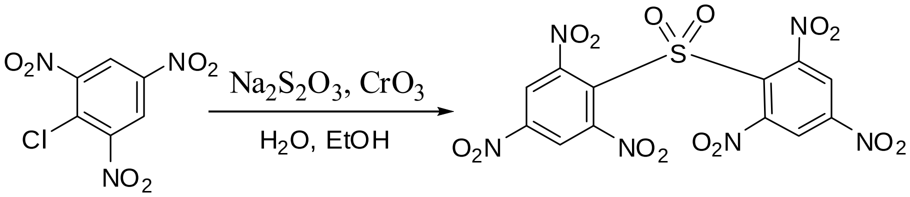


Figure 1.9. The synthesis of DIPSO using 2, 4, 6 - Trinitrochlorobenzene.

Hexanitrodiphenylamine (HEXYL) is another important high molecular weight polynitro benzene derivative having high thermal stability and performance. Its melting point is around 243 °C. It was first mentioned in the chemical literature in 1876 and as long ago as 1891 Haussermann drew attention to its explosive properties [55]. During the World War II, it was used in fusible composition with TNT for filling torpedos and marine mines [56]. Hexyl is a chemically stable compound. As van Duin and van Lennep found, it can withstand 30 days’ heating at 95°C. They also determined its initiation temperature as being 250°C, when heated at a rate of 5°C/min [57]. The standard laboratory synthesis of the hexyl involves treating 2,4-dinitrochlorobenzene with aniline to produce 2,4-dinitrophenylamine, followed by two-stage nitration (Figure 1.10) [58].

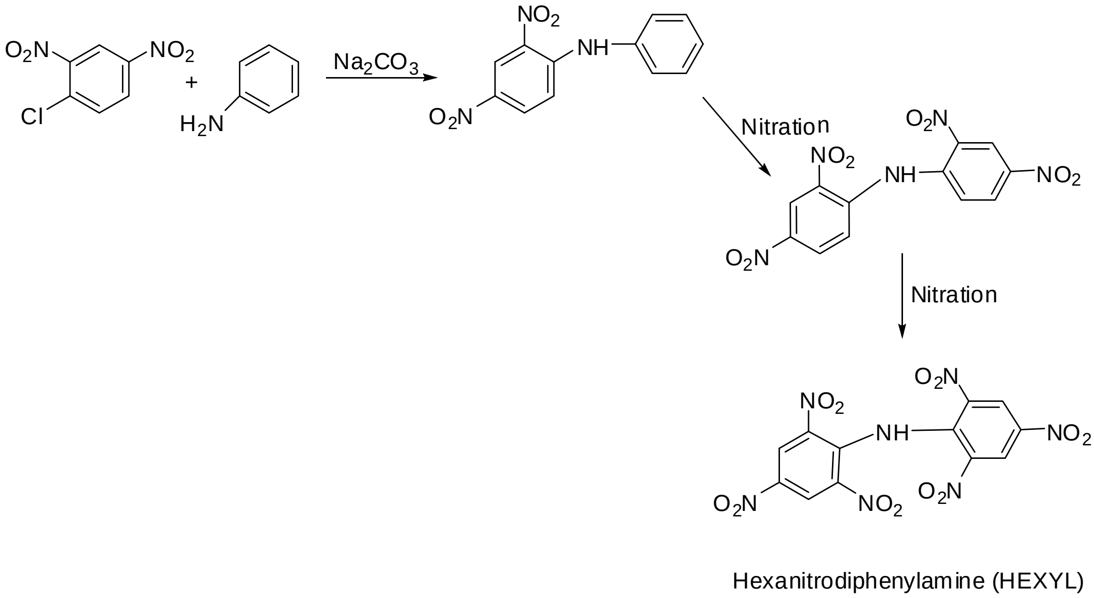


Figure 1.10. The synthesis of Hexanitrodiphenylamine (HEXYL).

Some high molecular weight aromatic compounds have been recognized for their high thermal stability. The reason is conjugation between aromatic rings. The conjugation between aromatic rings increases thermal stability. The -N=N- conjugation in Hexanitroazobenzene (HNAB) makes it good thermally stable explosives [59]. HNAB is reported as a very powerful and brisant high explosive. At a density of 1.77 g/cm^3, the detonation velocity is $7250ms^{-1}$ [60]. One method to synthysize HNAB is the treatment of picryl chloride with hydrazine, to obtain hexanitrohydrazobenzene. The hexanitrohydrazobenzene is further oxidized by nitric acid or nitrogen oxide gas in a glacial acetic acid solution to obtain HNAB (Figure 1.11) [61].

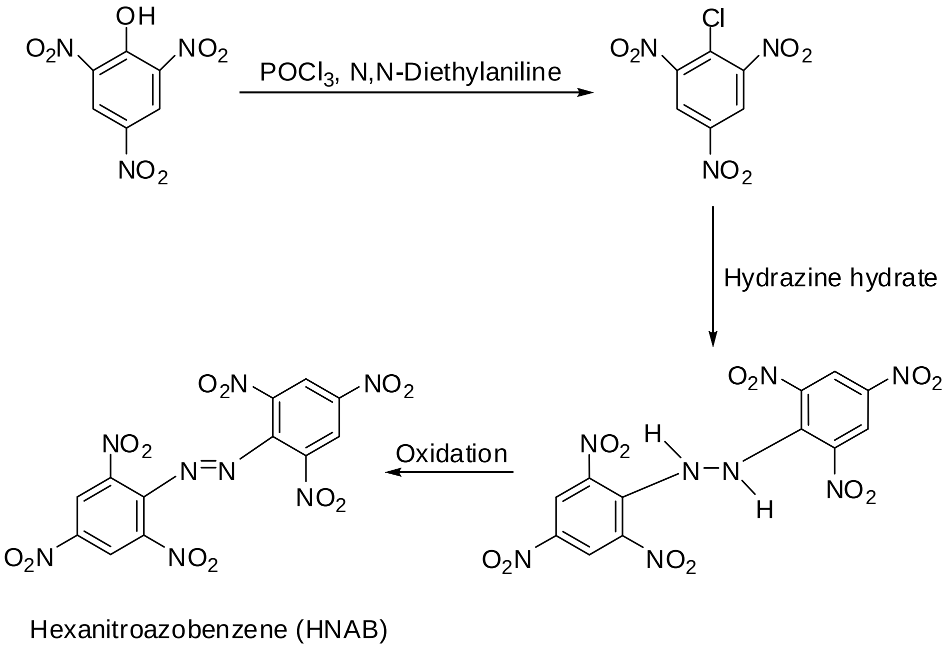


Figure 1.11. The synthesis of Hexanitroazobenzene.

1.4.1. Hexanitrostilbene (HNS)

HNS (2,2',4,4',6,6'-hexanitrostilbene) (Figure 1.12) is one of the most important example of conjugated high energy density materials. Its high thermal stability, high vacuum stability and superior resistance to sublimation at high temperature and low-pressure [62] make it a usefull energetic material. It is a powerfull explosive used in high performance explosive compositions and charges for use in demolitions and for use in missiles air to air and air to ground. HNS shows an impressive resistance to shock, pressure and friction even when heated at high temperatures.

Because of high melting point (304-308 °C) it has excellent thermal stability. This property makes it suitable for use in intercontinental balistic warheads, explosive bolts, ejection systems, artillery shells, rockets and high velocity tank-fired explosive projectiles [63]. For example, Iranian army uses HNS in warhead of SAHAP missiles

[64]. In the literature we see that it is used as crystal-modifying additive in melt–cast TNT [65].

HNS is also used in space exploration. HNS-TEFLON compositions were used as a rocket seperator in APOLLO missions [66]. Its high thermal stability also makes it usefull in petroleum industry. It is used in perforators for oilfield exploration [67].

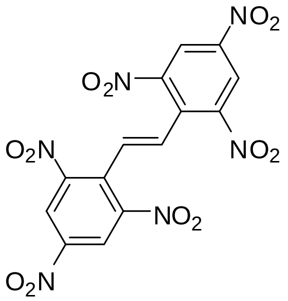


Figure 1.12. Hexanitrostilbene.

In UK, the plastic bonded explosive HNS/Kel-F800 95/5 was developed by Atomic weapons Research Establisment [68].

HNS first was synthesized by Shipp and Kaplan at US Naval Ordnance Laboratory (NOL) in 1964 [69]. They prepared HNS from 2,4,6-trinitrotoluene (TNT) and alkaline hypochlorite in tetrahydrofuran/methanol solution (Figure 1.13) [69]. The reaction is affected by temperature rise therefore the reaction must be carried at low temperatures (0-15 °C). After washing the red crude product with acetone and methanol yellowish HNS (Figure 1.14) is obtained. The yield of HNS produced by this method is low (30-35 % yield). In addition a lots of side products are formed during the reaction.

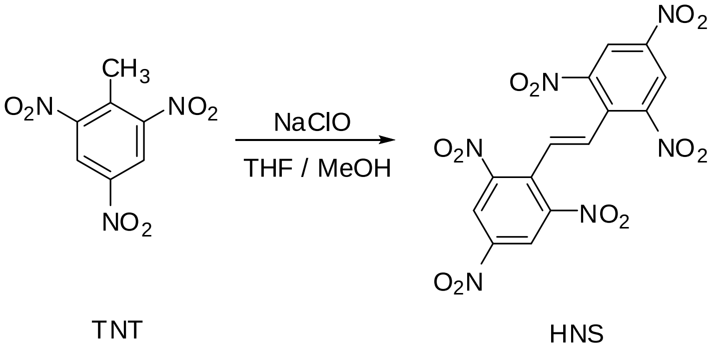


Figure 1.13. The synthesis of HNS by Shipp method.

Figure 1.14. Hexanitrostilbene.

In the reaction mechanism (Figure 1.15), TNT is initially deprotonated by hydroxide ion in the aqueous hypochloride solution then the chlorination gives trinitrobenzyl chloride. In the second part, trinitrobenzyl chloride formed is further deprotonated and attacked by trinitrobenzyl chloride. The C-C bond formed finally undergoes hydrogen chloride (HCl) elimination by base to form C=C double bond of HNS.

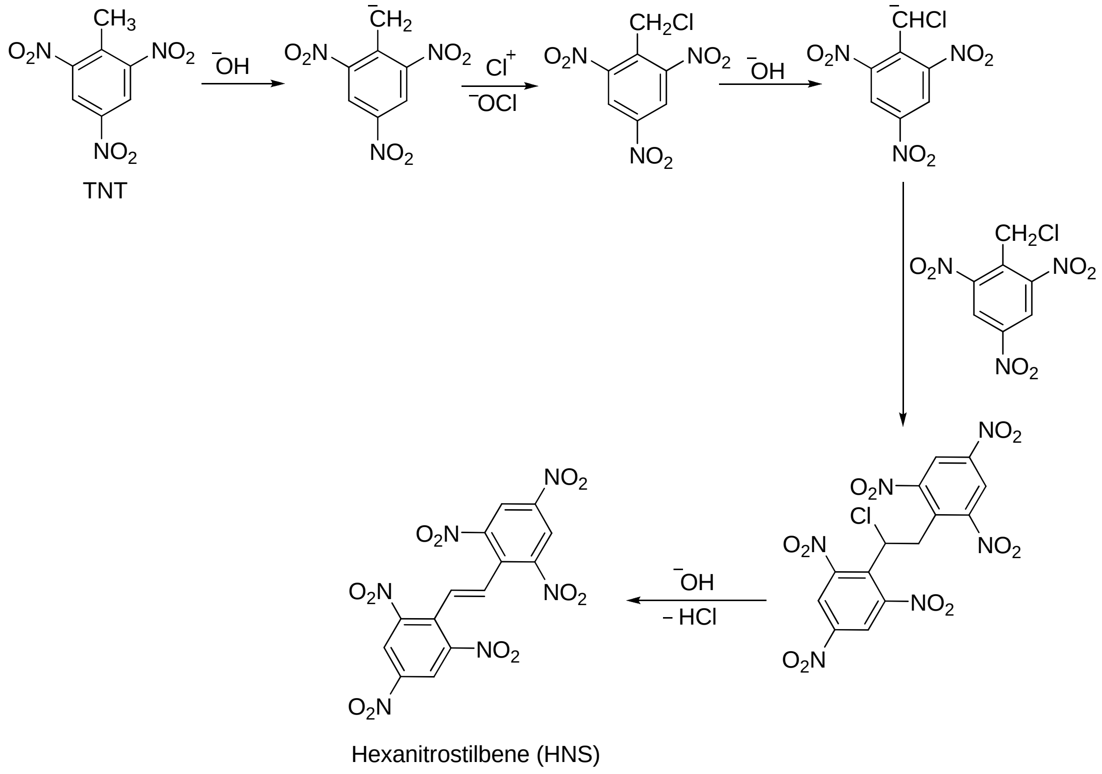


Figure 1.15. The synthesis of Hexanitrostilbene.

HNBB is the major by-product of HNS synthesis resulting due to medium basicity. In order to minimize this side reaction, TNT solution is slowly added to NaClO solution to decrease the possibility of reducing trinitrobenzyl chloride reacting with conjugate base of TNT [70]. HNS also can be obtained directly from trinitro benzyl chloride (TNBZCl) with higher yield by using nitrogen bases [71].

Another process to synthysize HNS was developed by Kompolthy et al. It consists of oxidative coupling of TNT in the presence of air. Methanolic potassium hydroxide solution with polar aprotic solvent (DMF, THF, DMSO…) and transition metal catalysts (Copper Sulfate, Cobalt naphthenate) are used (Figure 1.16). This procedure optionally could be used for the production of HNBB from TNT and HNS from HNBB [72].

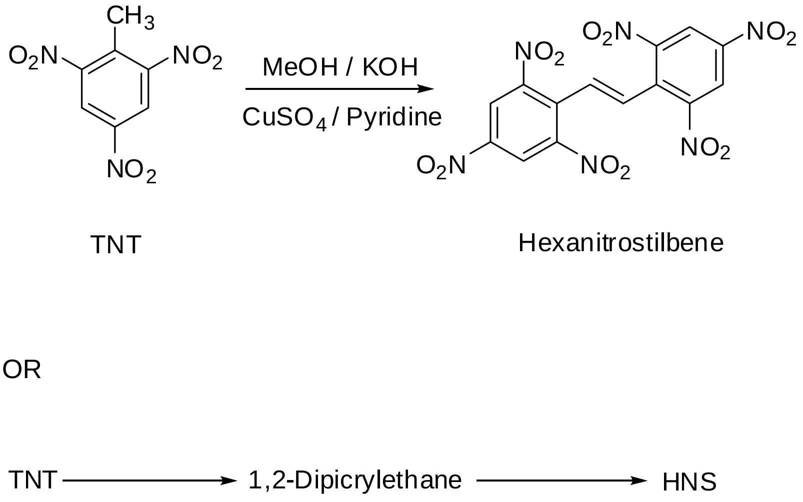


Figure 1.16. The synthesis of HNS by the Kompolthy method.

Although this process increases the yield a number of undesired byproducts formed in the final product. It is difficult to get high purity HNS with lower cost. Furthermore, removal of transition metal catalyst from the organic product and impossibility of recyling makes it inconvenient for large scale production [73].

Another process developed by Duffin et al., involves oxidation with oxygen in polar aprotic solvents with carboxyl group (Figure 1.17) [74]. However, this process also includes some problems. For instance, the time required to complete the reaction is too long (24-48 hours). Another disavantage is lots of side products are formed.

Impossibility of large scale production makes this process not feaseble for industrial application.

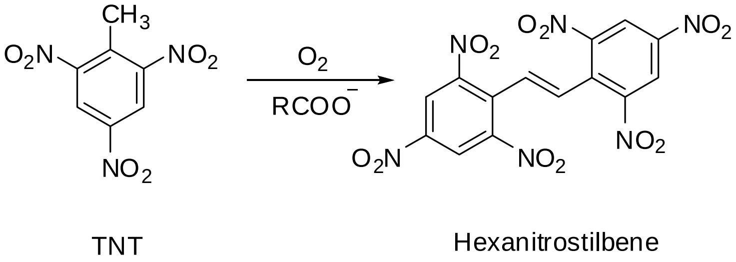


Figure 1.17. The synthesis of HNS by Duffin.

The last and recent procedure was developed by Bellamy and co-workers. Dissolving TNT in dimethyl sulfoxide (DMSO) with sodium benzoate then oxidizing with $CuCl_2$ gives 85 % HNS (Figure 1.18). Temperature of reaction must be 50-60 °C. Also passing air through the reaction medium increases the yield [75].

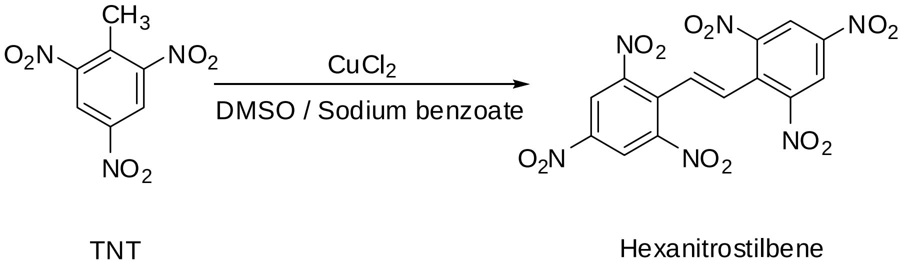


Figure 1.18. The synthesis of HNS by Bellamy.

Bellamy process faced with the similar problem like Kompolthy and Duffin's, such as high cost of the solvent and catalyst and inconveniance in large scale production.

1.5. AIM OF THE WORK

HNS as mentioned above refers to the strategical explosives for military and industrial applications. This research has been basically realized within the framework of SANTEZ Project (Project number: 000282.STZ.2008-1) that aims at the modernization of the armed forces in Turkey. The conditions for efficient HNS synthesis have been searched in order to get an efficient and economic ways of synthesis for Turkey.

In this SANTEZ project, the syntheses of HNS have been tried to be realized by means of the Shipp and TNT/benzoate processes. Due to its strategic military importance, many crucial points in its synthesis have remained unknown or obscure to scientific publicity which needs to be enlightened. These are solvent ratios, reaction temperature, NaClO concentration and amount, effect of solvent type, ways of addition of chemicals and formation of side product. These ambiguous points have been considered during this project, in whole or part.

In the second part of this project, a small scale batch reactor will be designed. This reactor will form the preliminary information for the large scale production in BARUTSAN ordinance factory.

CHAPTER 2

EXPERIMENTAL

2.1. MATERIALS

In this study solvents (Tetrahydrofuran, dioxane, dioxalane, methanol, dimethyl formamide, N-methyl pyrolidone) were purchased from MERCK. Oxidant (6 % of sodium hypochlorite solution) also was bought from MERCK and its concentration was checked from time to time. Trinitrotoluene (TNT) was supplied by Mechanical and Chemistry Industry of Turkey (MKEK).

2.2. SYNTHESIS OF HNS

2.2.1. Procedure 1

In a suitable beaker, 1.5 g of trinitrotoluene (TNT) was weighted and dissolved in 9 ml tetrahydrofuran (THF) stirred on a magnetic stirrer. After the dissolution of TNT completely, 12.5 ml methanol was added. Thereafter, the beaker was placed in 5 ^{o}C water. Once the temperature of above solution of TNT reached to 10 ^{o}C, it was slowly added to 10 ml cold 6 % NaClO solution while stirring rapidly. After all, TNT mixture was completely added, temperature of the mixture was maintained at 15 ^{o}C and kept at this temperature for about 90 min. with moderate stirring. When adding the TNT mixture in to the cold NaClO solution, red-brown mixtures were formed and temperature increased to 26 ^{o}C. During the mixing time, a red brown precipitate was formed. After 60 minutes, the mixture was poured into the mixture of 1ml sulfuric acid (H_2SO_4) with 100 ml of cold water. Sticky clays appeared on the surface. They were filtered off and washed firstly with 5 ml methanol and color changed to the cream-yellow, then washed with 3 ml acetone. The color of the final product was light yellow. Collected crystals of HNS were dried in an oven at 90 °C for about 1 hour. The yield was 0.57 g (38 %)

^{1}H NMR (400 MHz, D6-DMSO, 25 °C) δ 7.2 (2H, s), 9.2 (4H, s)
^{13}C NMR (100 MHz, D6-DMSO, 25 °C) δ 123.16, 126.16, 130.52, 147.05, 149.43
IR (**λ_{max}/cm^{-1}**)**:**3099, 1619, 1601, 1537, 1341, 1265, 1085, 957, 920, 776, 740, 722, 714, 684

2.2.2. Procedure-2

1.5 g of trinitrotoluene (TNT) was weighted in a suitable beaker. Then, 5 ml of dioxane was added and stirred until all the TNT dissolved.Then, 12, 5 ml of methanol was added. Dark yellow solution formed. After 10 minute of mixing, 1 ml of triethylamine was added. The beaker was placed in to water, having temperature of 20 °C. Thereafter, this mixture was slowly added to the 11 ml of cold 6 % NaClO solution. Dark red mixture was formed immediately after the TNT solution was added. Temperature rose to the 39 °C, and after 5-6 minute it was cooled down to the room temperature. Keeping at this temperature for about 60 min. with moderate stirring, precipitation formed. After that, the mixture was poured into the hydrochloric acid-water solution. The red-brown precipitates was collected on filter paper and washed with methanol to remove unreacted TNT and other side products and washed with acetone to remove hexanitrobibenzyl, another side product. After this washing step, light-yellow HNS crystals were collected and dried in an oven for two hours, 0.82 g (54 %) of HNS was collected.

Hexanitrostilbene
^{1}H NMR (400 MHz, D6-DMSO, 25 °C) δ 7.2 (2H, s), 9.2 (4H, s)
^{13}C NMR (100 MHz, D6-DMSO, 25 °C) δ 124.41, 127.40, 131.77, 148.22, 150.67
IR λ_{max}/cm^{-1}:3100, 1634, 1539, 1320, 1085, 920, 776, 740, 740, 722, 684, 631, 614

2.2.3. Procedure-3

1.5 g of trinitrotoluene TNT in 6 ml dioxalane was placed in a suitable beaker. The mixture was stirred to dissolve all TNT. After that, 12.5 ml methanol was added, and continuously stirred. 10 ml ice-cold 6 % NaClO was put into another beaker which was in 15 ^{o}C-water equipped with a magnetic stirrer. Afterwards, TNT solution was added slowly to the NaClO. The color of the mixture suddenly changed to red-brown. Temperature of the mixture increased to 38 ^{o}C and after 8 minutes it dropped to 25 ^{o}C. At the end of constant stirring for 80 minute, the mixture was poured into the mixture of 1 ml hydrochloric acid (HCl), 1ml nitric acid (HNO_3) and 150 m cold water. Precipitated dark red substance was collected by filtration, and then washed with 3 ml methanol and finally with 2 ml acetone. After drying the crystals of HNS in an oven at 90 ^{o}C for two hours, 0.73 g (49 %) light yellow HNS crystals were obtained.

Hexanitrostilbene

^{1}H NMR (400 MHz, D6-DMSO, 25 ^{o}C) δ 7.2 (2H, s), 9.15(4H, s)

^{13}C NMR (100 MHz, D6-DMSO, 25 ^{o}C) δ 124.41, 127.40, 131.77, 148.22, 150.67

IR (λ_{max}/cm^{-1}):3100, 1638, 1545, 1317, 1078, 917, 779, 737, 730, 720, 680, 626, 610

2.2.4. Procedure-4

1 g of TNT in 25 ml dimethylsulfoxide (DMSO) was placed in 100 ml beaker. The mixture was stirred to dissolve all TNT.Then, 2.2 g of sodium benzoate and 0.9 g of anhydrous cupper (II) chloride ($CuCl_2$) were added into the flask equipped with magnetic stirrer at room temperature (25 ^{o}C). The color of the mixture slowly changed into red. After 10 hours of mixing, the mixture was poured into 100 ml of water. A yellow-cream precipitate formed. The precipitate was filtered off and washed with water to remove the unreacted cupper (II) chloride and washed with

methanol to remove the unreacted TNT. After drying in an oven at 90 °C for two hours, 0.58 g (58 %) of HNS was collected.

Hexanitrostilbene

^{1}H NMR (400 MHz, D6-DMSO, 25 °C) δ 7.2 (2H, s), 9.15(4H, s)

^{13}C NMR (100 MHz, D6-DMSO, 25 °C) δ 124.0, 126.20, 130.13, 149.9, 152.14

IR (λ_{max}/cm^{-1}): 3103, 1624, 1610, 1530, 1318, 1243, 1082, 920, 776, 734, 714, 680

2.3. CRYSTALLIZATION OF HNS

2.3.1. DMF Crystallization

0.5 g of HNS in 15 m of dimethylformamide (DMF) was put into a flask equipped with a magnetic stirrer. After complete dissolution at 40 °C, the bright purple solution formed. In another flask, 150 ml ice-water was prepared. All of the HNS solution was injected into ice-water with an injection syringe. A cream-yellow precipitate was formed. Then, the precipitate was filtered off and washed with methanol. After drying it in an oven at 90 °C for two hours, 0.4 g (80 %) high purity good crystalls of HNS were obtained.

2.3.2. NMP Crystallization

0.5 g of HNS was put into 10 ml of N–methyl pyrolidon (NMP) at room temperature (25 °C). Temperature of the mixture was gradually increased to 150 °C. In the meantime, HNS was dissolved. Then, temperature was decreased to room temperature with cold water. HNS crystals precipitated during this time. All procedure was repeated 3 times again. After that, the crystals formed at room temperature were filtered and washed with cold water. The final product was high purity good crystals of HNS. 0.42 g (84 %) high purity good crystalls of HNS were obtained.

2.4. SENSITIVITY TEST

2.4.1. Impact Sensitivity Test

This test aims to determine the impact resistance of energetic materials. Approximately 0.04 cm^3 HNS was employed. Centering plate was placed in the middle of hole of the ring gear (Figure 2.1). The test sample was placed into hollow steel cylinder (chamber). After that, this hollow cylinder and cylindrical steel bar was placed in the middle of the ring gear. Protective chassis cover was closed and air fan run. The weight to be applied was attached to the device's slide and raised. Thereafter, the lever on the weight was pulled to the right to open the lock and test started. Reactions observed for the lowest energy value were set as limiting value. When the six of the samples were tested, it should not give reaction at one step below this limiting value.

Figure 2.1. The impact sensitivity test apparatus.

2.4.2. Friction Sensitivity Test

This test is to determine frictional resistance of energetic materials. Approximately 0.01 cm^3 volume of HNS was used. Porcelain friction pin was fit into the slot and fixed to the device (Figure 2.2). The surface line on porcelain friction plate should be perpendicular to the friction direction. Test material was placed on the porcelain friction plate below the porcelain pin. Thereafter, weight was determined from load table and it was attached to one of the distance on loading arm (I, II, III, IV, V, VI) (Picture). Finally, with activation of device, the friction process was started.

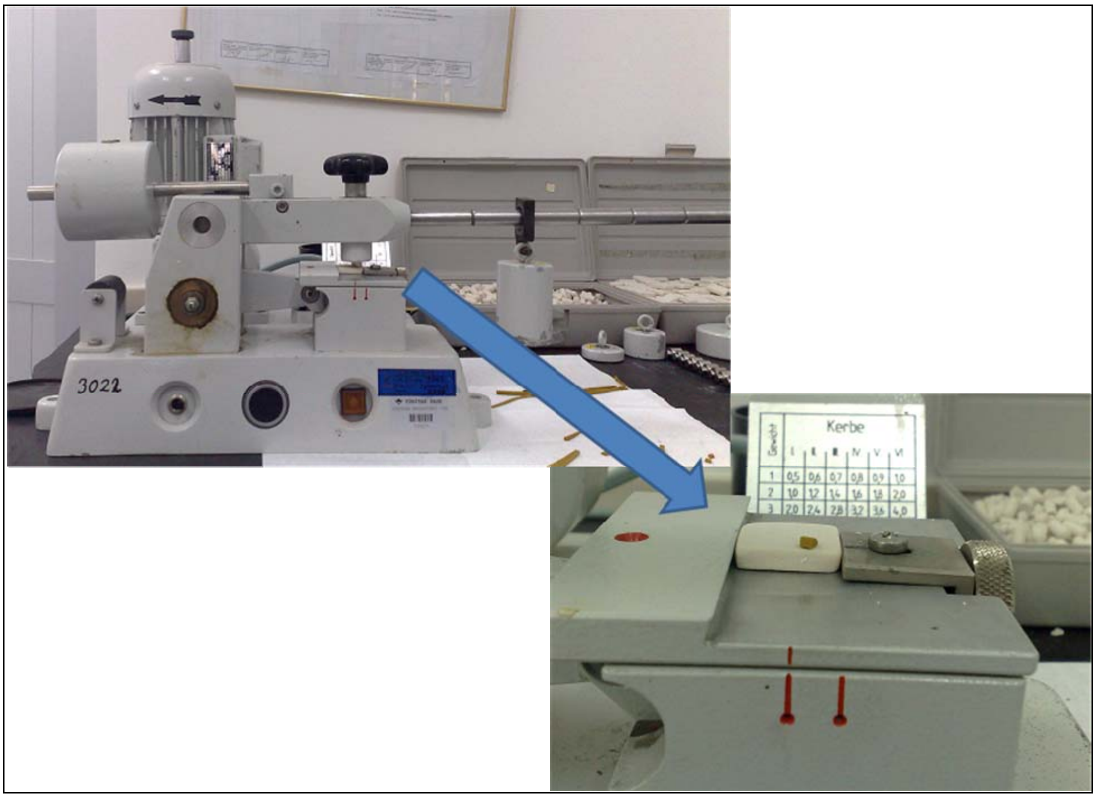


Figure 2.2. The friction sensitivity device.

2.5. HNS ANALYSIS

2.5.1. Spectroscopic Analyses

2.5.1.1. Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded on a Bruker DPX 400. Chemical shifts are reported in ppm relative d_6-DMSO (^{1}H: δ=2.5), d_6-DMSO (^{13}C: δ=40.0) and TMS as internal standards.

2.5.1.2. Fourier Transform Infrared Resonance Spectroscopy (FTIR)

FTIR spectra were taken by Perkin Elmer Spectrum 100 FTIR spectrometer FTIR to clarify the structural information of HNS.

2.5.2. Scannig Electron Microscopy (SEM)

The SEM (Figure 2.3) is an instrument that produces a largely magnified image by using electrons instead of light to form an image [76]. A finely focused electron beam scanned across the surface of the sample generates secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by detectors to form images of the sample displayed on a cathode ray tube screen [76].

In this study, SEM picture of HNS crystals was taken by METU Central Research Laboratory with QUANTA 400F Field Emission (Figure 2.3)

Figure 2.3. Scanning Electron Microscopy.

2.5.3. Thermal Stability Analysis

2.5.3.1. Differential Scanning Calorimeter

Differential scanning calorimeter or DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature [77]. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic exothermic processes or changes in heat capacity [78]. In this study DSC analysis was made by TÜBİTAK-SAGE to estimate the melting point and decomposition temperature of HNS.samples Perkin Elmer Diamond DSC (Figure 2.4) was used for this purpose.

Figure 2.4. Differential Scannig Calorimetry (DSC).

2.5.3.2. Thermo gravimetric Analysis (TGA)

In a Thermo gravimetric Analysis, the percent weight loss of a test sample is recorded while the sample is being heated at a uniform rate in an appropriate environment [79]. Thermo gravimetric curves (thermograms) provide information about the composition of the sample, decomposition points of explosives, and solvent residues [80]. Perkin Elmer Pyris 1(Figure 2.5) TGA device at TÜBİTAK-SAGE was used to get thermograms of HNS.

Figure 2.5. TGA device.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1. HNS SYNTHESIS WITH NaClO OXIDATION

During this project, hexanitrostilbene was synthesized on the basis of Shipp procedure. This procedure was selected because of four reasons. The first one is the availibilty and reusability of solvents. Tetrahydrofuran (THF), dioxane or dioxalane was used as the main solvent. They are all available and cheap. In addition they can be recycled after the reaction. The second reason is the use of sodium hypochlorite (NaClO) as an oxidant. Sodium hypochlorite (NaClO), known as bleaching agent, could be produced easily and cheaply in large portion. Methanol is used as a co-solvent to mix TNT solution with sodium hypochlorite in this procedure. Also the availibilty and low cost of methanol are the other advantages of this procedure. The fourth and last reason of using this procedure is its applicability on large scale production. The literature shows that HNS could be synthesized at large scale only with this procedure. In the UK and China, there are two production plants on the basis of Shipp procedure.

Although there are lots of advantages of this procedure, there are equally some problems in its application. The most important one is the low availability of information about procedure because of the strategical importance of HNS as mentioned before. The low yield is another problem faced with. The last problem is the purification and bulk density of HNS. The raw product of HNS involves lots of side products. These are hexanitrobibenzyl (HNBB), trinitrobenzyl chloride (TNBCl) and some unreacted TNT. Also the bulk density of HNS should be increased to apply.

The aim of this study is to solve all problems mentioned above. Firstly, works are done to ease the part of the procedure. These are the effects of temperature, the solvent type, solvent amount, effect of the sodium hypochlorite (NaClO) amount and pH change to determine reaction end time.

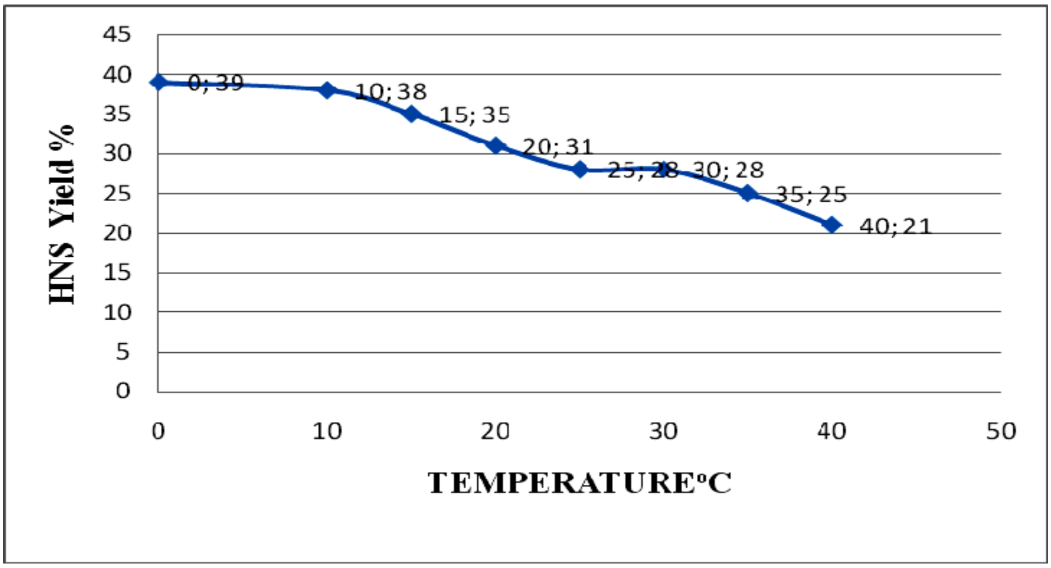
In the second part of the study, the work was carried out to solve the problem of purification and bulk density. The experiment showed that washing raw HNS with methanol and acetone eliminates impurity. In addition to this, crystallization of HNS was done for further purification and high bulk density. Two crystallization procedures were designed for this purpose. One of them was dimethylformamide (DMF) crystallization, and the other was N-methyl pyrolidone (NMP)

On the basis of this information, three procedures have been designed to synthysize HNS. Procedure-1 was designed from orginal Shipp procedure. The unidentified parts of Shipp procedure were identified. Procedure-2 and procedure-3 were the modified versions of the Shipp procedure to solve the problem mentioned above. The solvent type, reaction temperature, solvent amount, sodiumhypochloride amount and reaction end time were changed to get high yields of HNS.

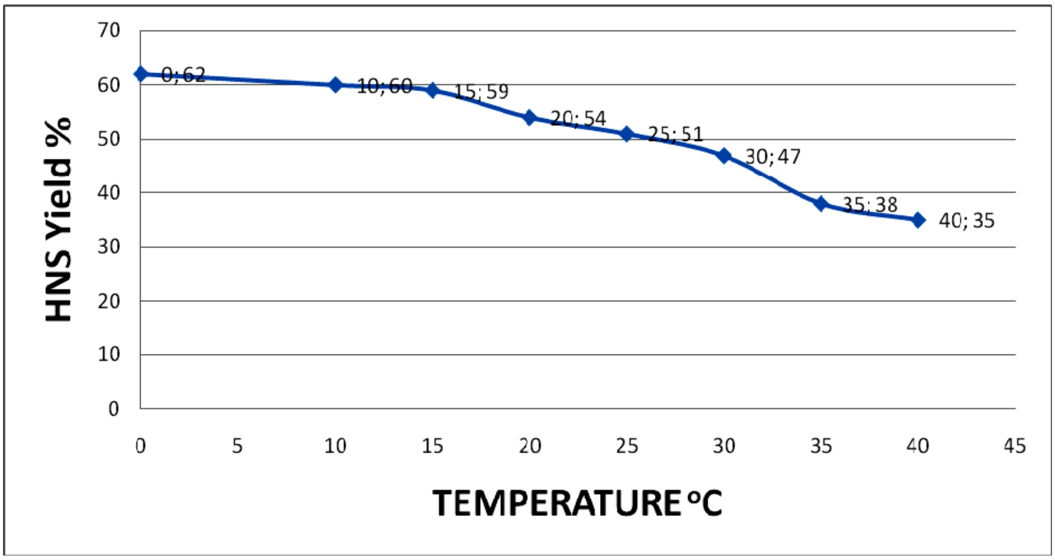
Finally, the spectroscopic (NMR, FTIR), thermal (DSC, TGA) and sensitivity (impact, friction) analyses were carried out to characterize HNS produced by these three procedures.

3.1.1. Effect of Temperature

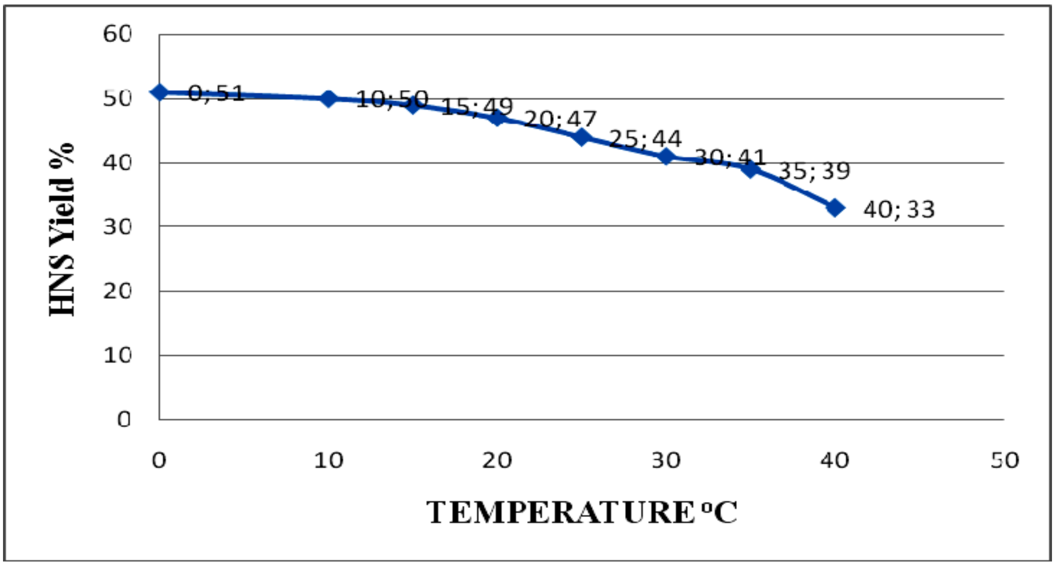
The effect of temperature on three procedures is shown in Figure 3.1. The reaction was carried out for eight different temperature grades from 0 ^{o}C to 40 ^{o}C. The yield was calculated after each temperature. As reaction temperature increases, the HNS yield decreases for all procedures. Although the effect of increasing temperature was similar for each procedure, the rate of decreasing was different. For procedure-1, the yield was decreased 15 % when increasing reaction temperature from 0 ^{o}C to 25 ^{o}C. For procedures-2 and -3 this change was 11 % and 7 %, respectively. For all procedures, there was a small error for yield resulting from ısolation of HNS from reaction media.



Procedure-1



Procedure-2



Procedure-3

Figure 3.1. The changes of HNS yield vs. temperature for Procedures 1-3. First number at data point is temperature (^{o}C) and second one is percent yield (%).

3.1.2. Effect of Solvent Type

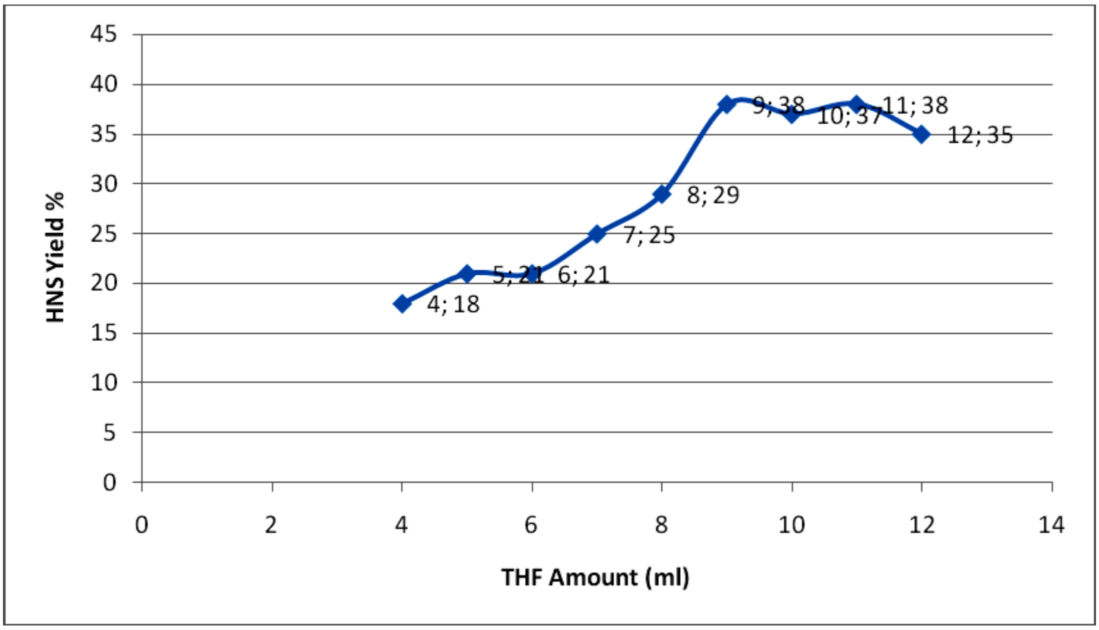
As a result of our review of the literature and experiments, the importance of solvent selection has been realized. Various attempts were made on alternative solvents. According to the results, the solvent used in the reaction must be polar aprotic. Originally tetrahydrofuran (THF) was used to synthesize HNS. However, THF has some disadvantages. These are, the high volatility and flammability, peroxide formation and bad odor. To overcome these problems, different solvent systems were tried. Solvents which could dissolve TNT were selected. These are acetone, ethyl acetate, chloroform, dioxane, dioxalane. According to the results, it was observed that using 1,4- dioxane and dioxalane (Figure 3.2) instead of THF solved problems arising from THF system. In addition, those solvents lead to a significant increase in the yield of HNS formation.

(A) (B)

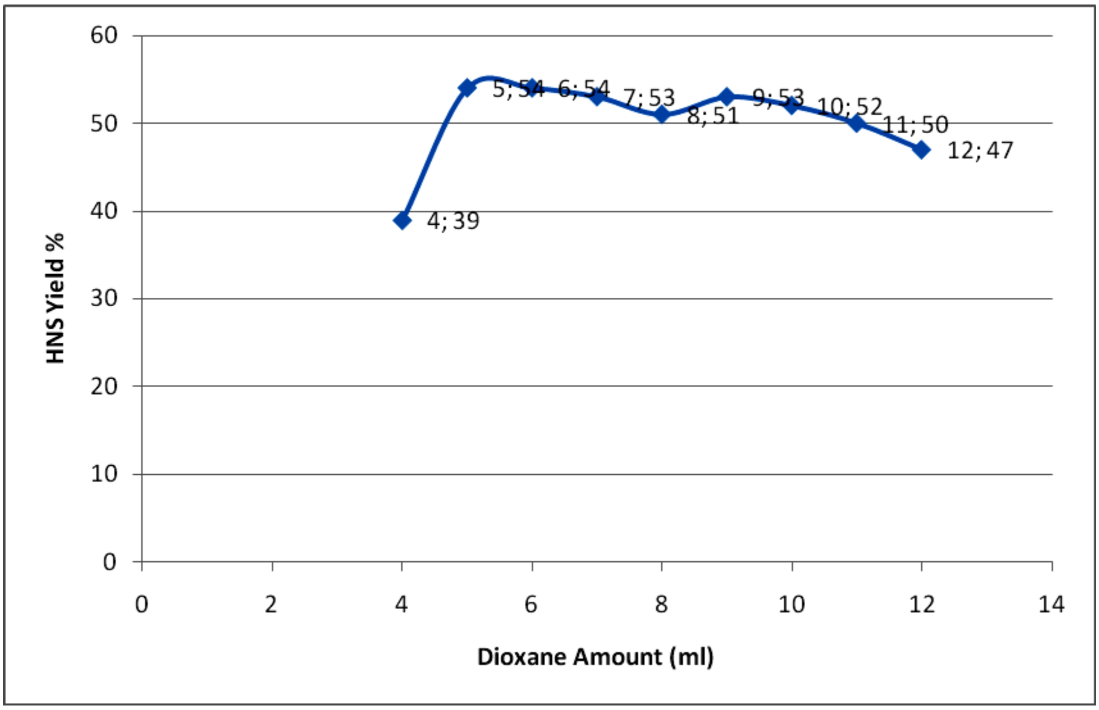
Figure 3.2. (A): 1, 4 - Dioxane, (B): 1, 3 - Dioxalane.

3.1.3. Effect of Solvent Amount

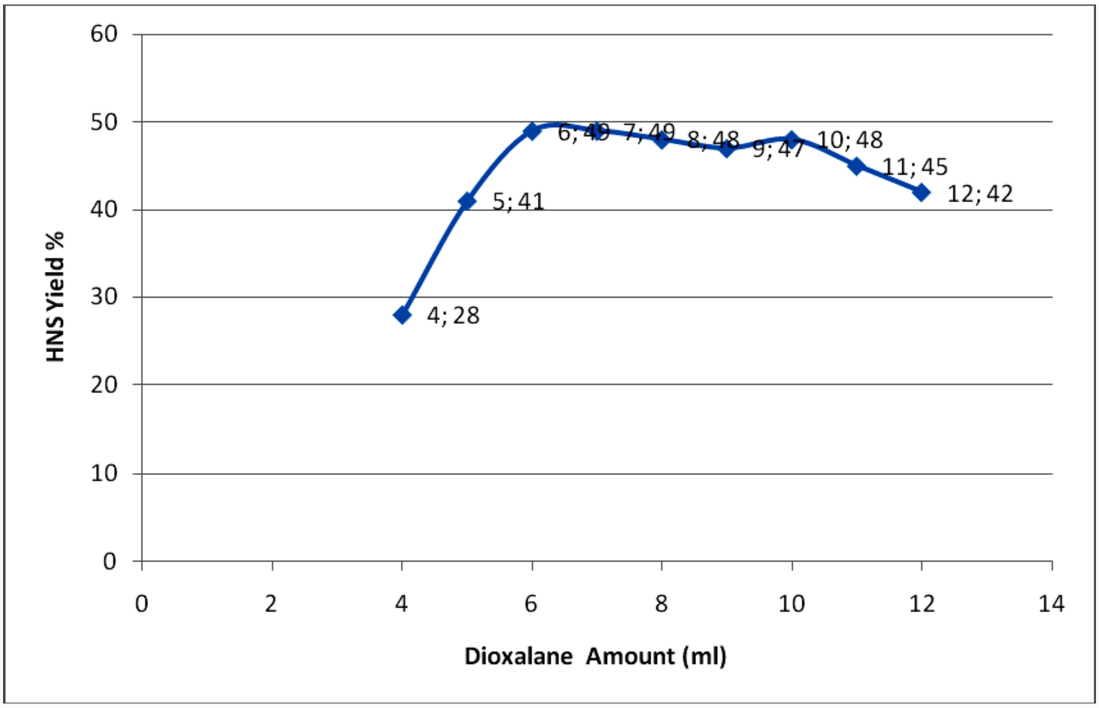
The effects of solvent amount on reaction yield for procedures 1-3 are seen in Figure 3.3. In the experiments performed to explore the effect of the solvent amount, starting from 4 ml up to 12 ml nine different test kits designed to estimate effect of it on HNS yield. For 1.5 gr of TNT, maximum yield for procedure-1 was obtained by using 9 ml THF. The maximum yield was obtained in 5 ml dioxane for procedure-2 and in 6 ml dioxalane for procedure-3.



Procedure-1



Procedure-2



Procedure-3

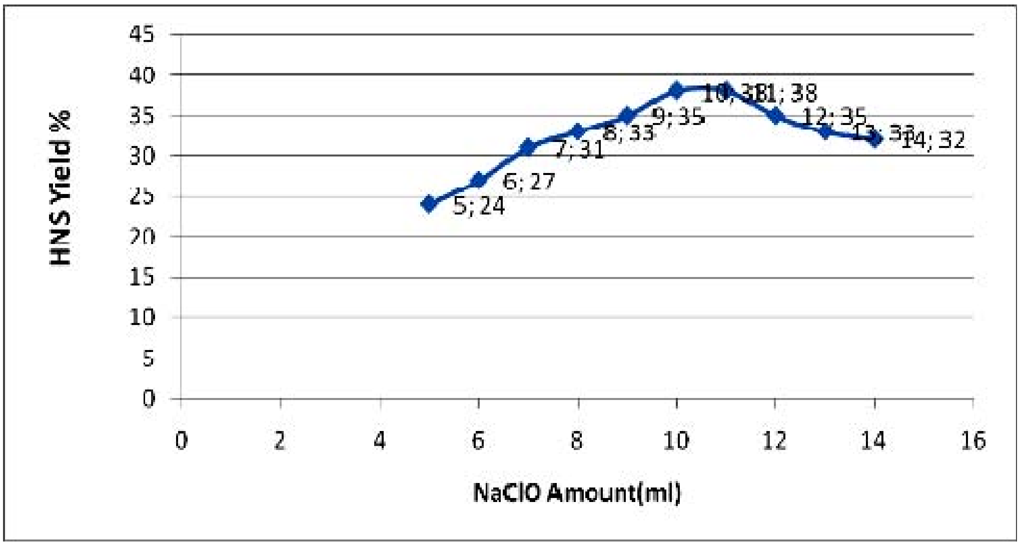
Figure 3.3. The change of HNS yield vs. solvent amount for Procedures 1-3*.

* For 1.5 g TNT.

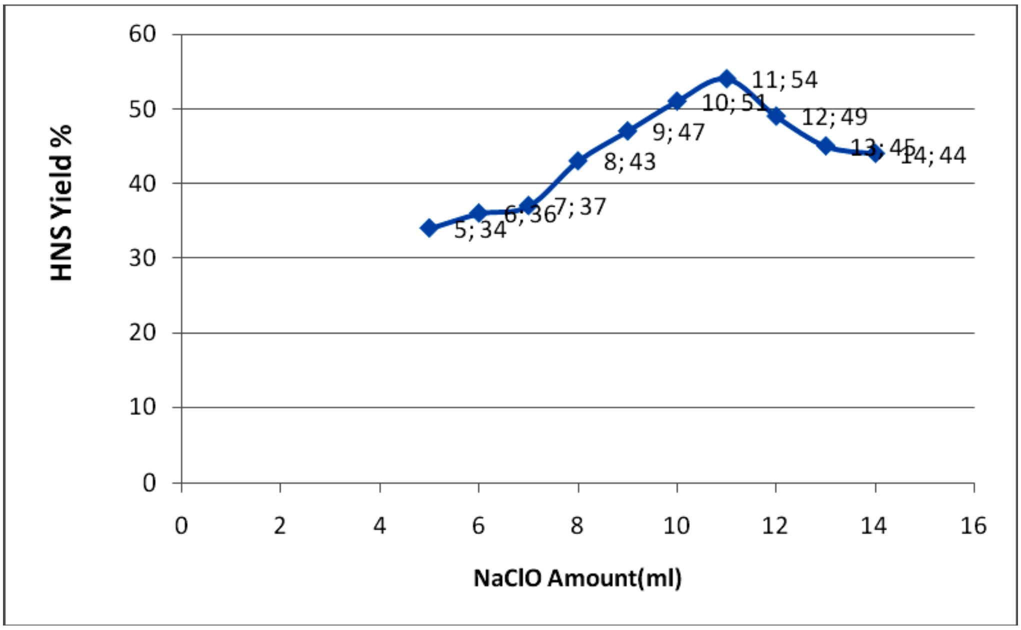
* Reaction temperature for Procedures 1-3 were 5 °C, 20 °C and 15 °C, respectively.

3.1.4. Effect of NaClO Amount

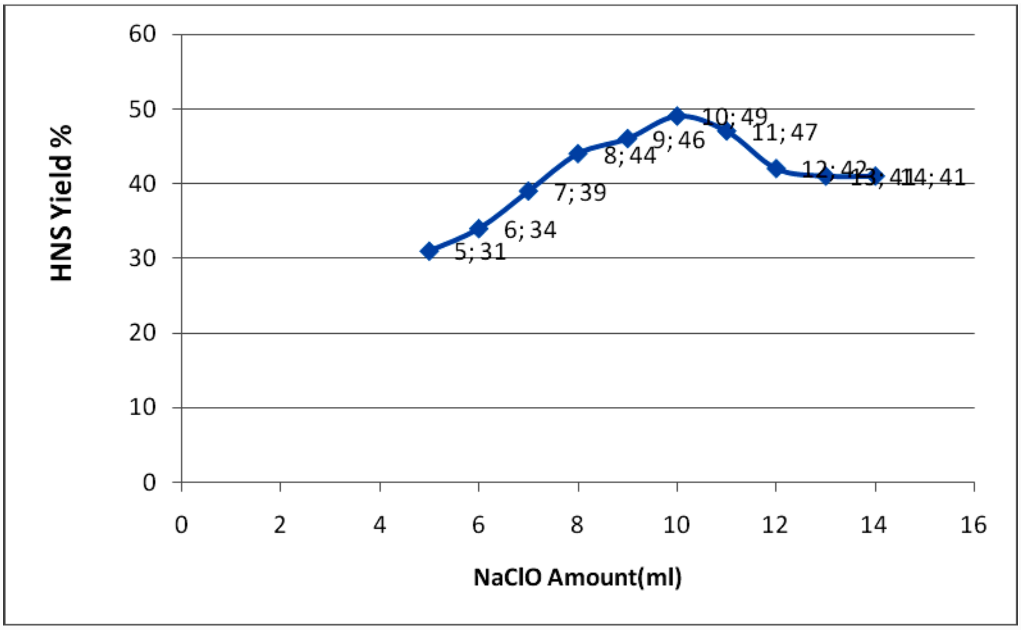
Sodium hypochloride (NaClO) used in HNS synthesis acts as an oxidant as well as a base. Because of these functions, the effect of NaClO amount is very critical and important for the production of HNS. 6 % NaClO was used in this work. In optimized temperatures and solvent amount, reaction was carried out for ten different NaClO amount from 5ml to 14 ml. The Figure 3.4 below shows the effect of increasing NaClO amount on HNS yield.



Procedure-1



Procedure-2



Procedure-3

Figure 3.4. The changes of HNS yield vs. the amount of sodium hypochloride (NaClO) for Procedures 1-3.

According to the graph, all three procedures show similar behaviour towards NaClO amount. Generally for 1.5 g of TNT and using 5-11 ml NaClO, HNS yield increased. It has been observed that after the addition of 11 ml of NaClO, HNS yield starts to decrease. Procedures 1-3 gave the maximum yield for 10 ml NaClO. On the other hand, Procedure-2 gave maximum yield when 11 ml of the hypochloride was used.

3.1.5. pH Change

Sodium hypochloride increases the bacisity of the reaction medium. The reaction mechanism, as mentioned above, shows that at the end of coupling reaction (Figure 3.5) HCl formation occurs and decreases the pH. From this point of view, we have made an assumption that if we find time that pH decreasing stops; we take this time as the reaction end time.

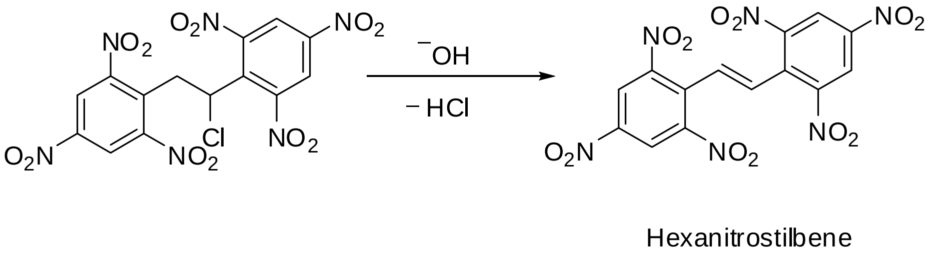
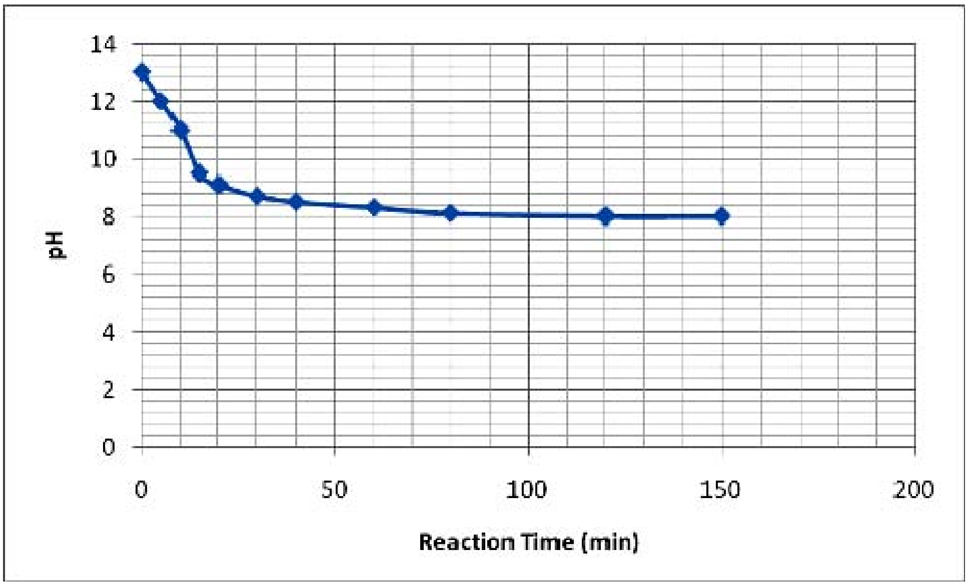
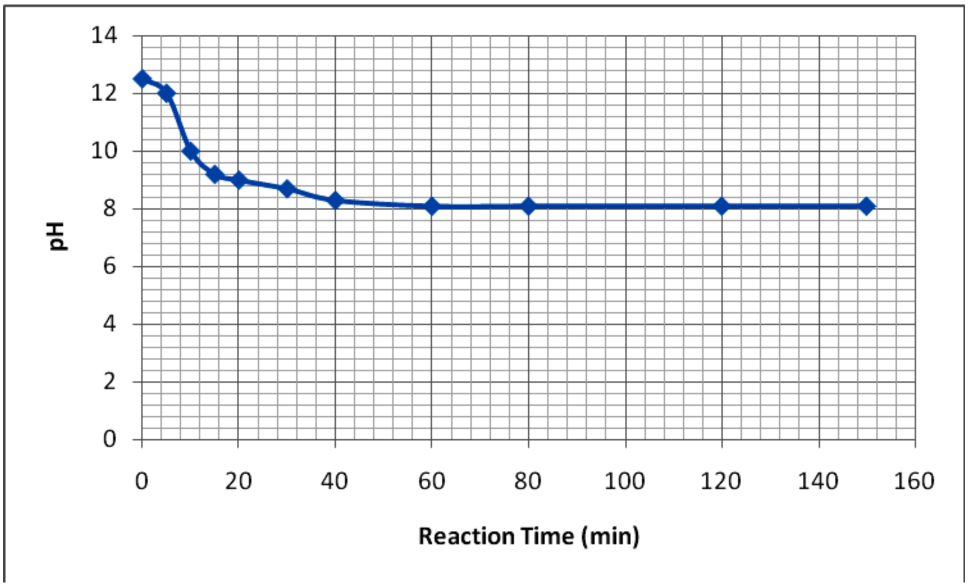


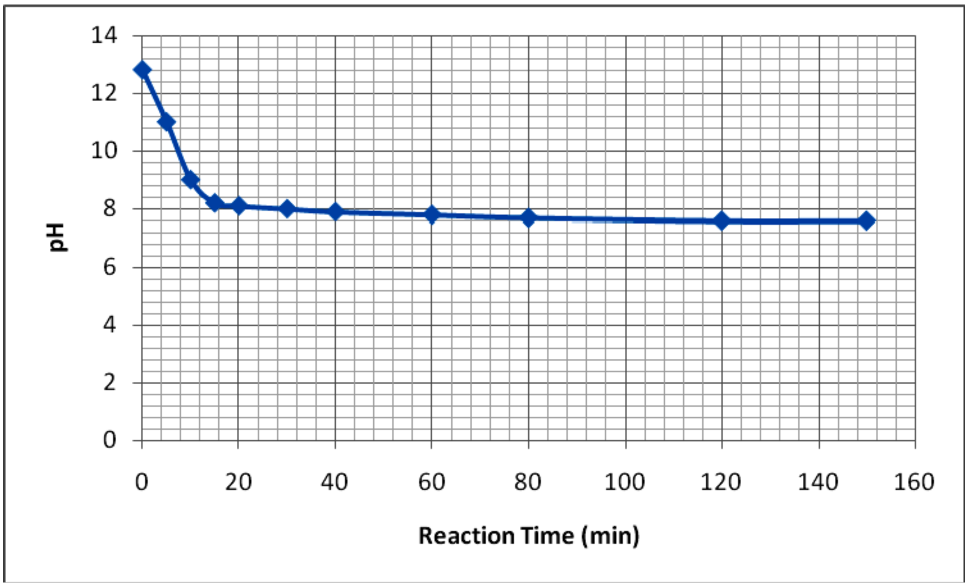
Figure 3.5. The HCl formation in HNS synthesis.



Procedure-1



Procedure-2



Procedure-3

Figure 3.6. The pH change vs. time for Procedures 1-3.

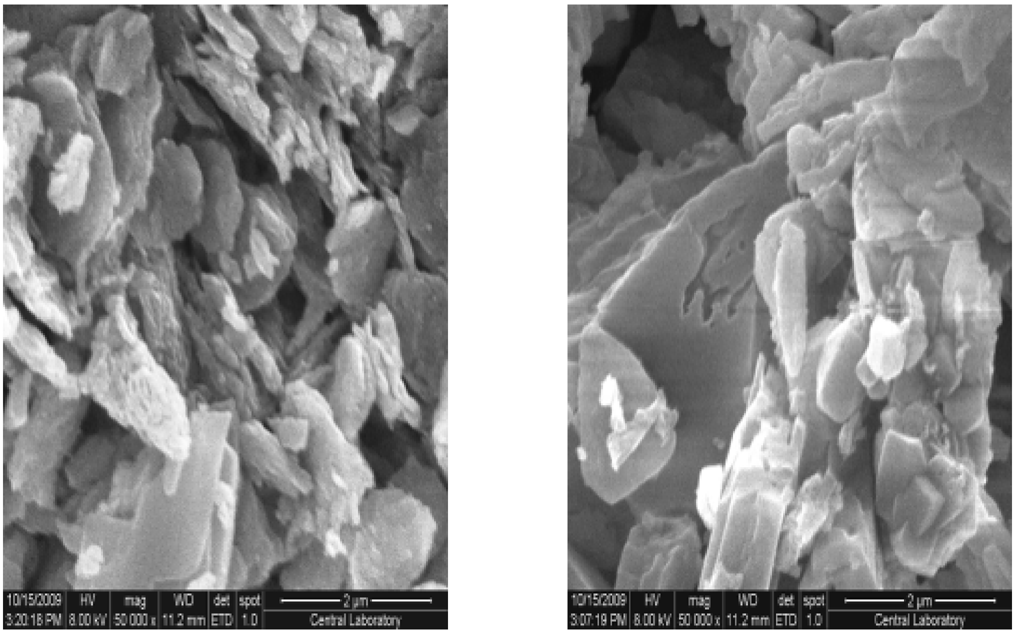
According to the results as shown in (Figure 3.6), pH of the solution after mixing NaClO with TNT solution immediately increased then decreased. After that reaction, the pH reached to a steady value. This point for procedures (1, 2, 3) was 120, 60, 80 minutes, respectively. As a result, the reaction end time was decided according to these values.

3.2. HNS CRYSTALLIZATION

The raw product of HNS has less purity and low bulk density [81]. The scientist put considerable effort to get high purity and high bulk density HNS [82]. While several recrystallization methods for this purpose have been developed [83], many of them, because of strategical importance, lack sufficient details about their applicability on raw HNS. Another limitation of recrystallization was the low solubililty of HNS in many organic solvents. DMF, HNO_3, NMP and, to some extent, acetonitrile are the solvents that could dissolve HNS [84]. Recrystallization from 90 % HNO_3 is widely used in the manufacture of high purity and high bulk density HNS. Although it is relatively cheap and easy to perform, the resulting product is contaminated with nitric acid [85]. In another and recent process dimethylformamide and N-methylpyrolidone was used to recrystallize HNS [86]. Using these two solvents, two different recrystallization processes were developed.

3.2.1. DMF Crystallization

In DMF crystallization, firstly, HNS was dissolved completely in 50^{o}C dimethylformamide. After that, this purple solution was sprayed to the cold water. The cream colored precipitate was formed. Filtering and drying this precipitate gave high purity and high bulk density HNS. The scanning electron microscope (SEM) picture of raw product (A) and final product (B) are seen in Figure 3.7

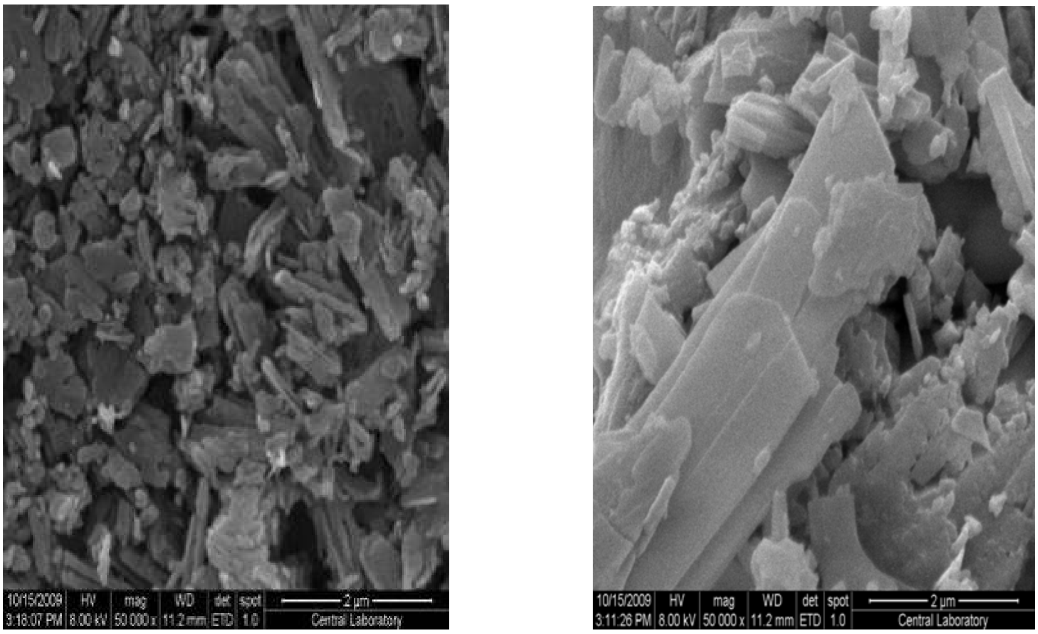


(A) (B)

Figure 3.7. SEM micrographs of HNS, (A): before recrystallization, (B): after recrystallization in DMF.

3.2.2. NMP Crystallization

N-methyl pyrolidone (NMP) was also used as a recrystallising solvent for HNS [87]. Bellamy et al, reported that NMP used for recrystallization increased the bulk density, heat resistancy and improve handling characteristics [88]. NMP at room temperature has low dissolving capacity. With increasing temperature, this capacity increases. To recrystallize HNS, it initially was added to NMP, and then temperature of this mixture was gradually increased to 150 ^{o}C. At this point, all HNS dissolved completely. After which, the solution was cooled down to the room temperature (25 ^{o}C). This procedure was repeated three times again. At the end of last cooling, all the mixture was poured into ice-cold water. The final product was high purity HNS. The SEM pictures (Figure 3.8) also show the improvement in bulk density.



(A) (B)

Figure 3.8. SEM micrographs of HNS, (A): before recrystallization, (B): after recrystallization in NMP.

3.3. HNS CHARACTERIZATION

HNS characterization was made with different methods. Firstly spectroscopic analyses were done by Nuclear magnetic resonance (NMR) and Fourier Transform Infrared Resonance Spectroscopy (FTIR). Secondly, thermal analysis were done to see the effect of temperature on HNS with differential scanning calorimetry (DSC) device and thermal gravimetric analysis (TGA) device. Thirdly and finally, the friction and impact sensitivity towards explosion were calculated by impact sensitivity and friction sensitivity device**.**

3.3.1. Spectroscopic analysis

3.3.1.1. Nuclear Magnetic Resonance spectroscopy

^{1}H-NMR and ^{13}C-NMR spectra of HNS were investigated in d_6-DMSO, and chemical shifts (δ) were given relative to tetramethylsilane as the internal Standard. HNS has two different (Figure 3.9.) protons: the olefinic protons and the phenyl protons.

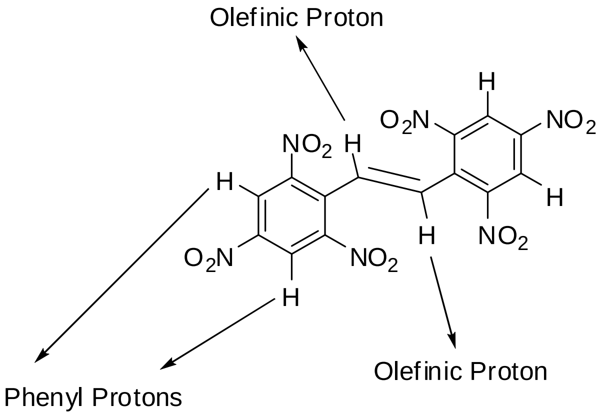
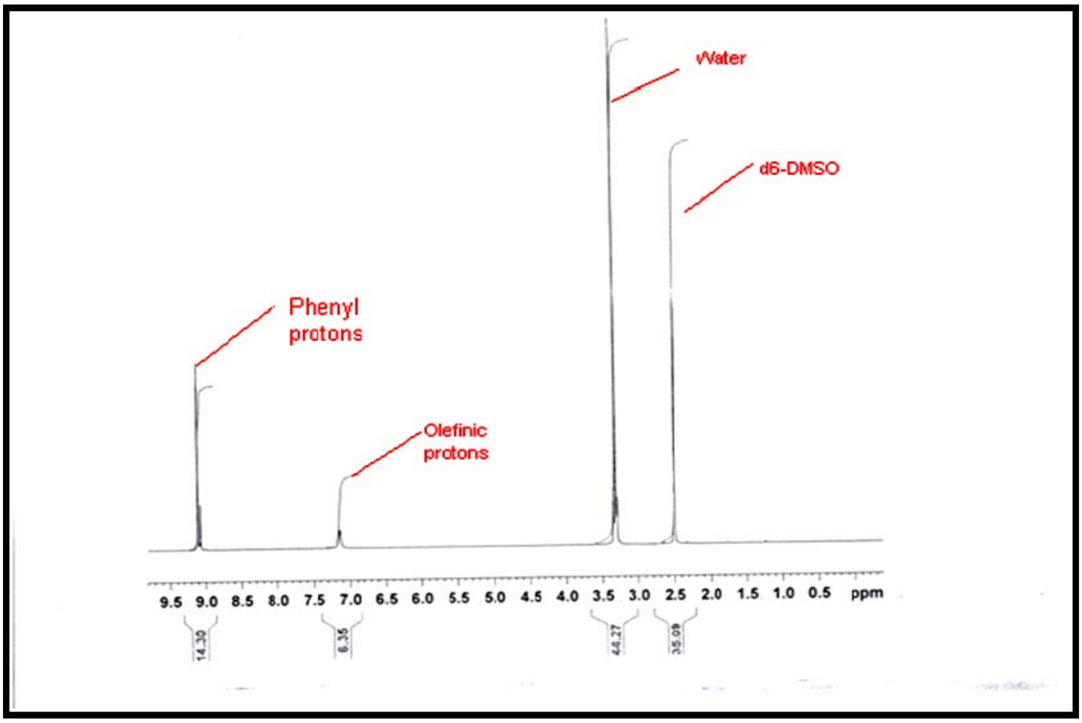
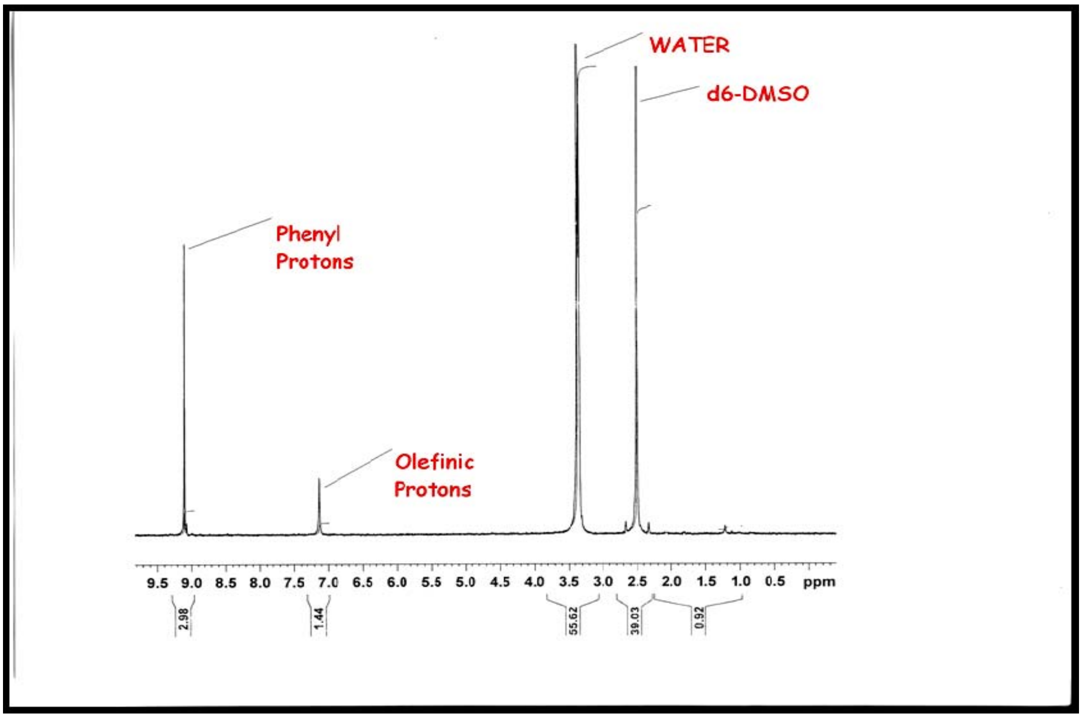


Figure 3.9. Two different protons of Hexanitrostilbene.

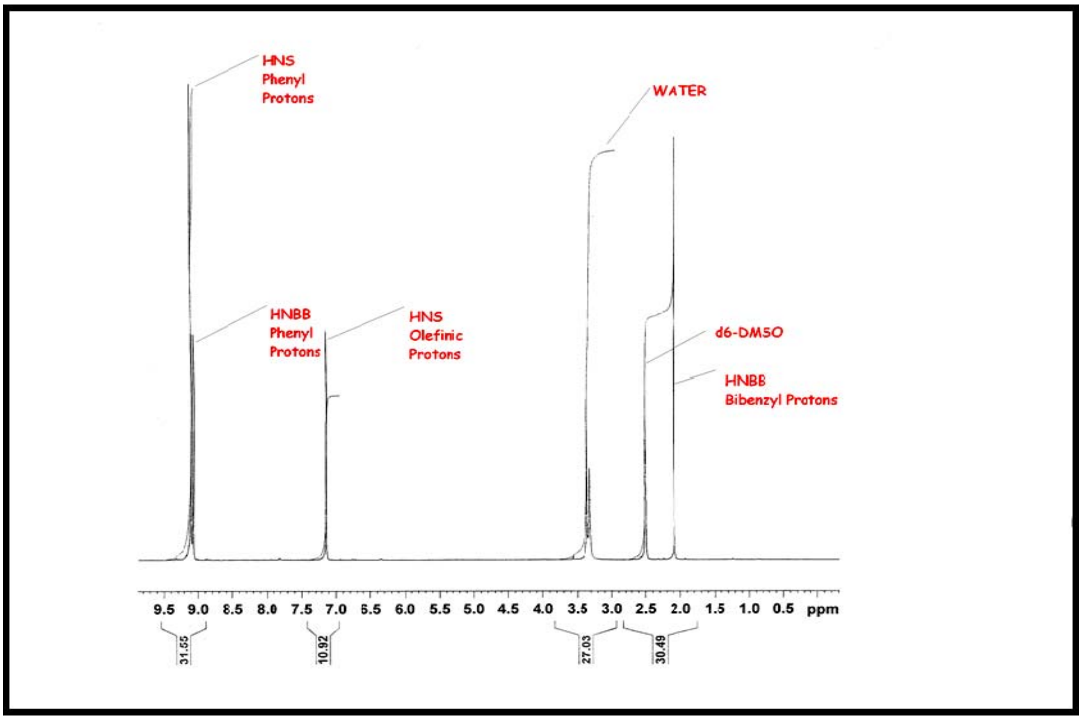
As seen in ^{1}H-NMR spectrum (Figure 3.10) below, olefinic protons occur between 7.1-7.3 ppm and phenyl protons are at 9.1-9.2 ppm.



Procedure-1



Procedure-2



Procedure-3

Figure 3.10. ^{1}H-NMR spectra of Procedures 1-3.

^{1}H-NMR spectra of the products procedures-1 and-2 show pure HNS with very little side product. On the other hand, in procedure-3 20-25 % hexanitrobibenzyl (HNBB) (Figure 3.11) formation was observed. Although explosive properties do not change, thermal stability decreased as a result of HNBB formation [89].

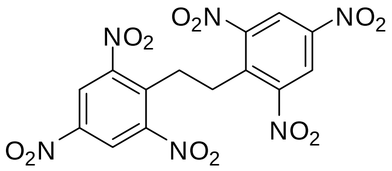
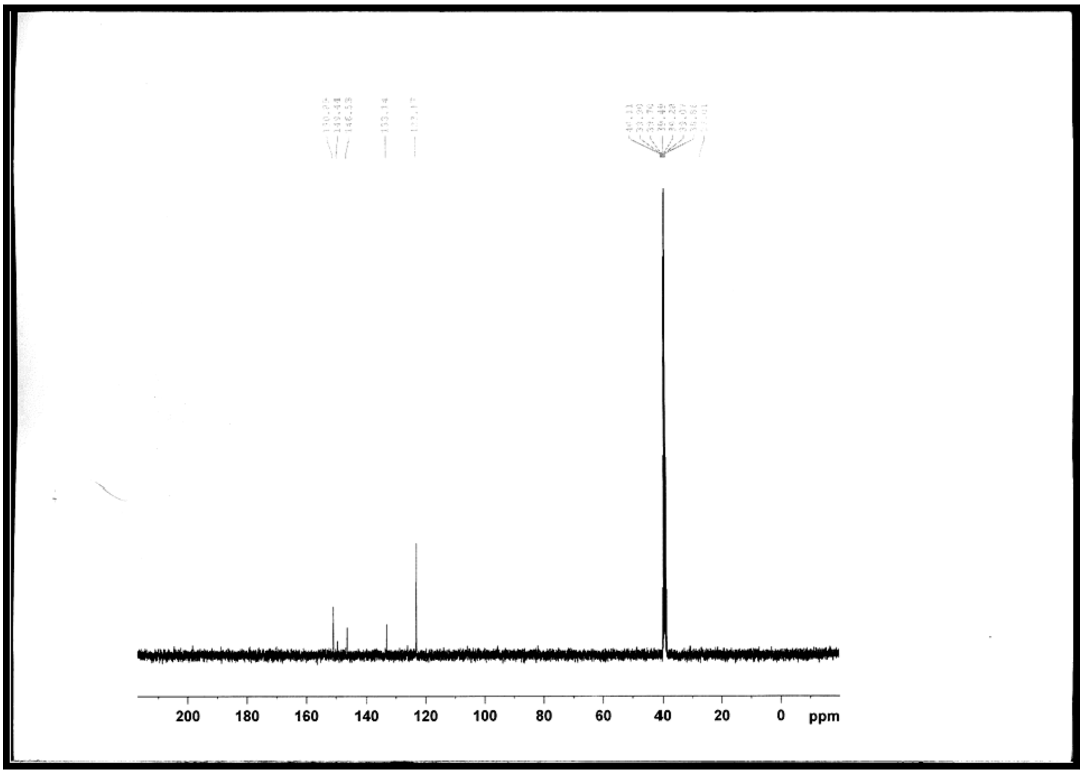
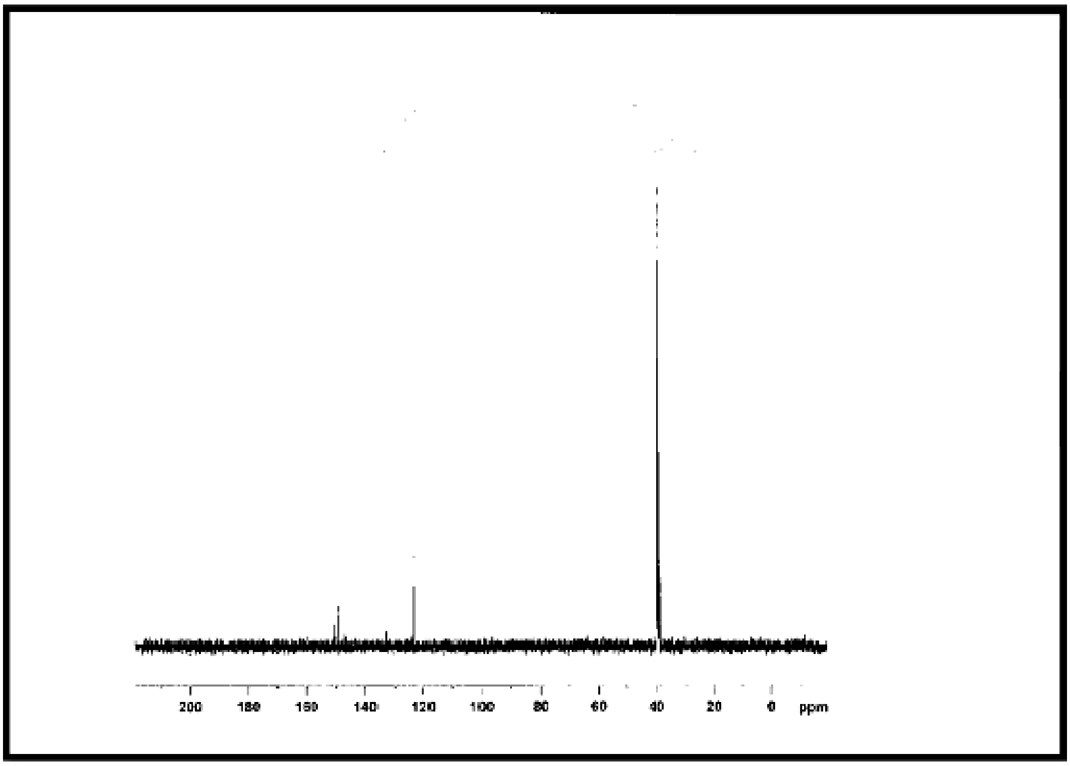


Figure 3.11. Hexanitrobibenzyl (HNBB).

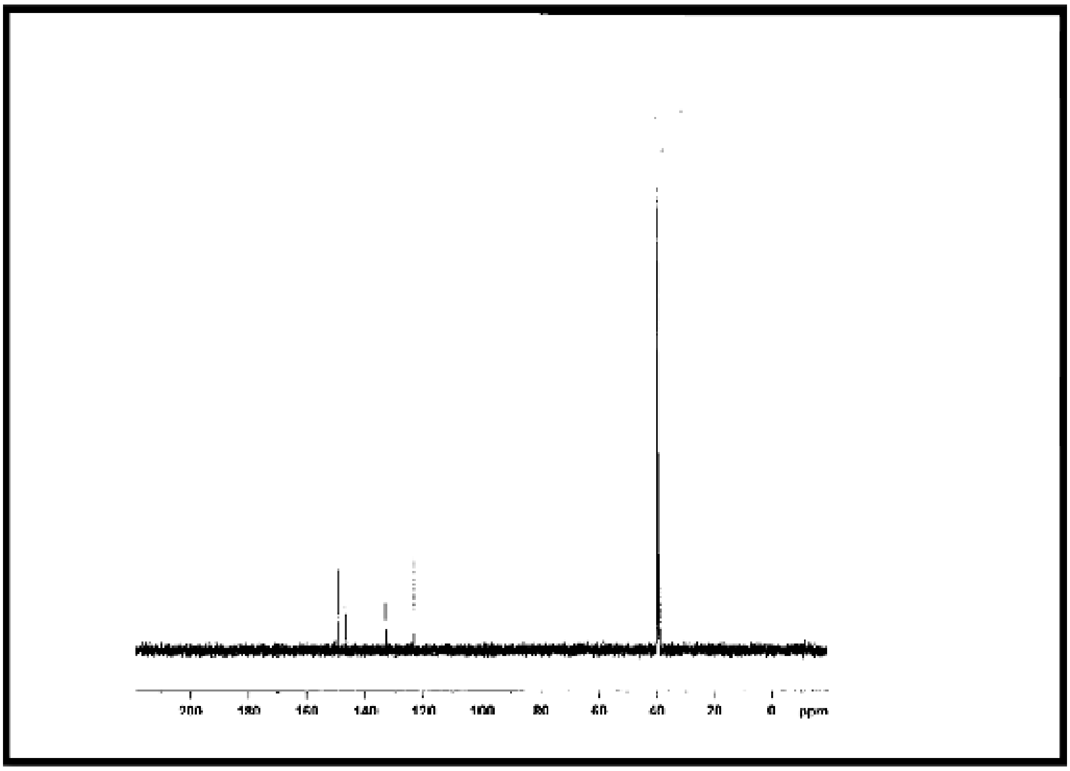
^{13}C-NMR results are given in Figure 3.12. HNS has five different C atoms; therefore, in ^{13}C-NMR there must be 5 different peaks. As seen below, there are 5 different ^{13}C peaks. These results also show the HNS formation with high purity.



Procedure-1



Procedure-2

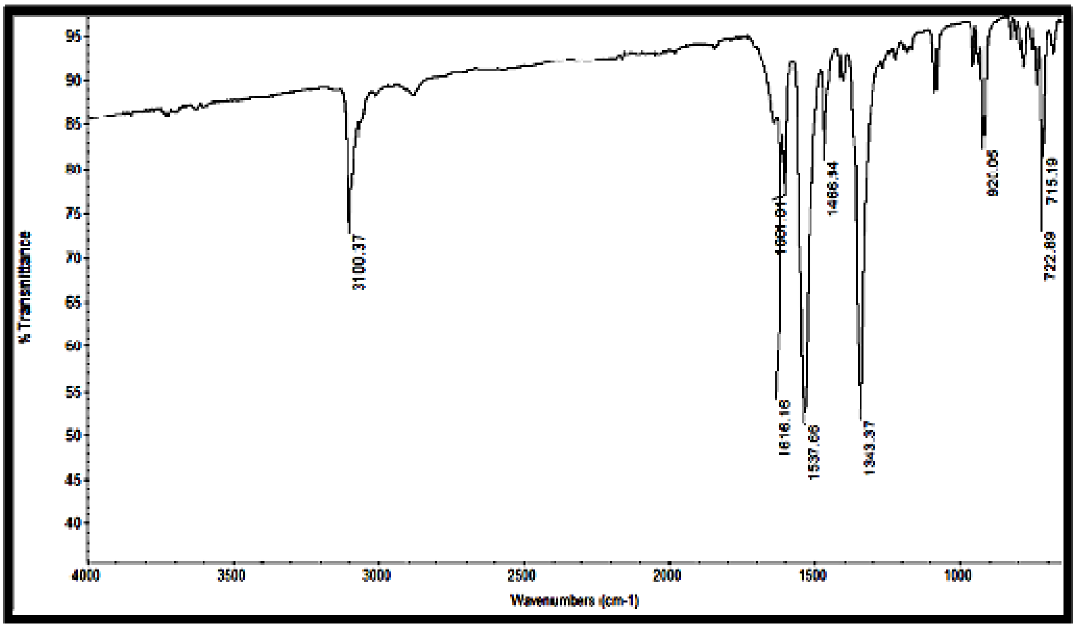


Procedure-3

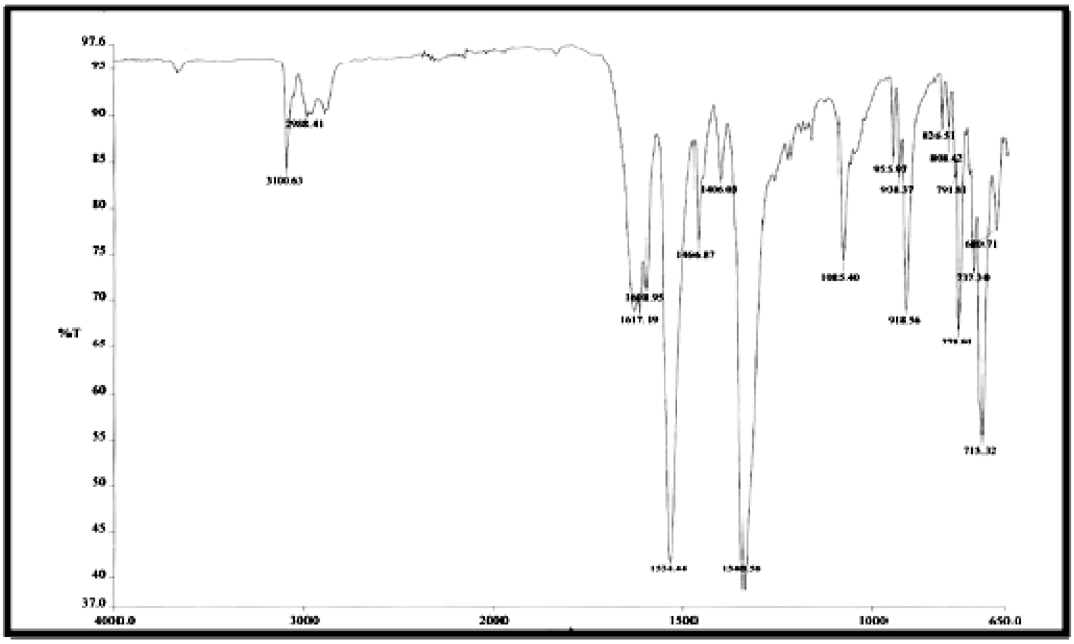
Figure 3.12. ^{13}C-NMR spectra of Procedures 1-3.

3.3.1.2. Fourier Transform Infrared Resonance Spectroscopy

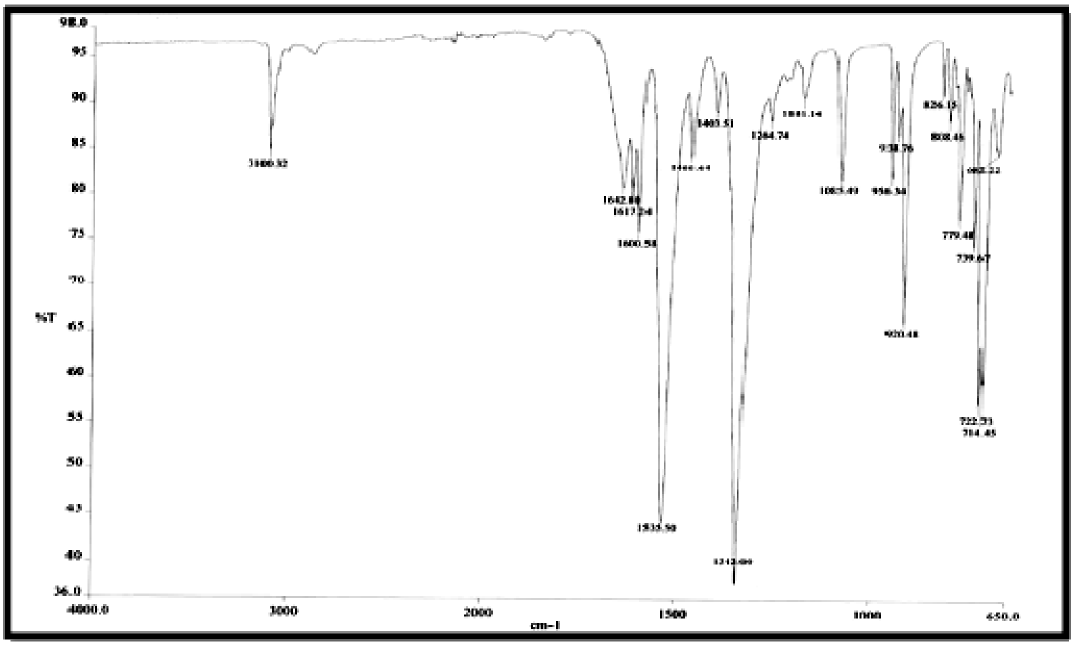
FTIR spectra were taken by Perkin Elmer Spectrum 100 FTIR spectrometer. FTIR results of HNS synthysized by three procedures (Procedures 1-3) are given (Figure 3.13.) Strong and sharp band was observed due to the –=CH- stretching at 3100 cm^{-1}.



Procedure-1



Procedure-2



Procedure-3

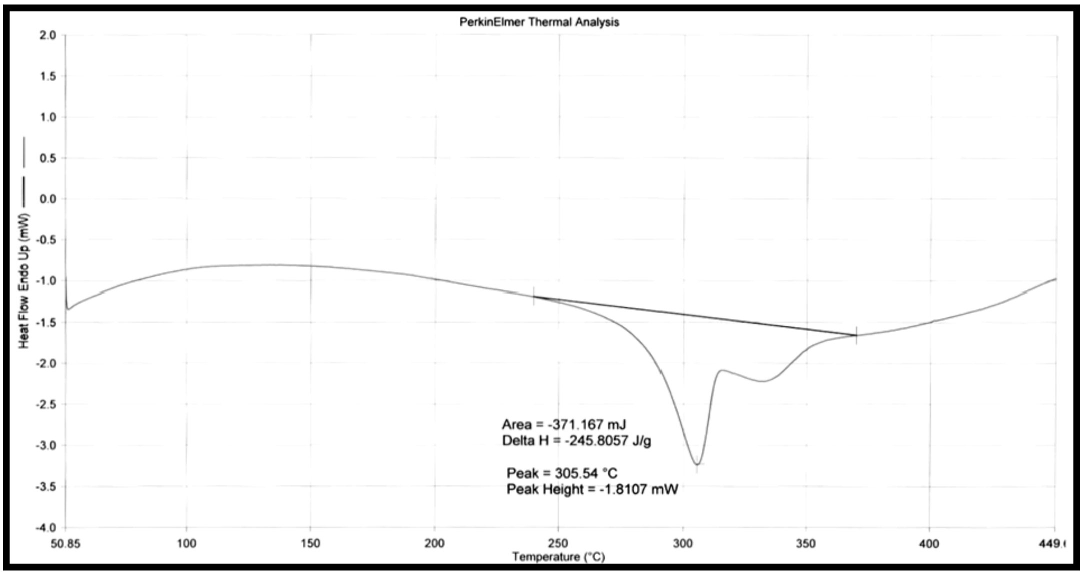
Figure 3.13. FTIR spectra of Procedures 1-3.

3.3.2. Thermal Analysis

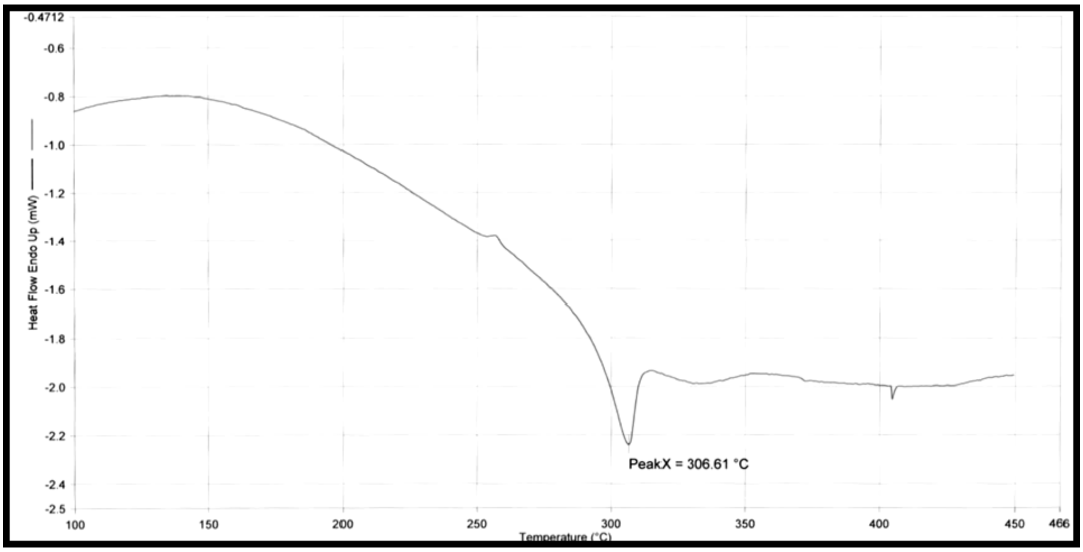
Hexanitrostilbene is known as highly thermally stable compound. Even at temperatures as high as 200-300 ^{o}C, it still conserves its stability and just a little decomposition occurs. This property makes it a strategically important explosive for critical miltary and space applications, as mentioned before. Therefore, thermal properties of HNS produced by three procedures (Procedure 1-3) gain importance and must be analyzed to get high quality HNS. The thermal analysis of products was made by Perkin Elmer Diamond via differential scanning calorimetry (DSC) and Perkin Elmer Pyris 1 Thermogravimetric Analysis (TGA) devices.

3.3.2.1. Differential Scanning Calorimetry

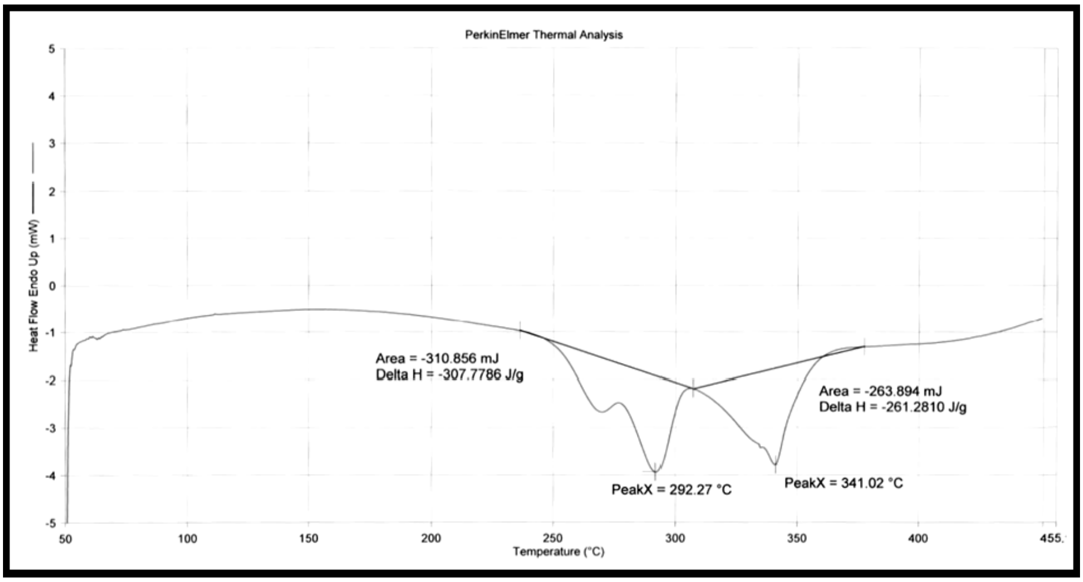
Differential scanning calorimetry (DSC) gives detailed information about thermal stability, melting point and decomposition behavior of a sample [79]. Actually any reaction or transformation involving absorbtion or release of heat can be detected with DSC [79]. In Figure 3.14, DSC analyses of HNS obtained from three products (Procedure 1-3) were given. HNS gives strong exotherm between (300-310 ^{o}C) [79]. The DSC results of HNS produced by three processes (Process 1-3) are consistent with the literature. HNS from procedure-1 gave strong exothermic peak at 305.54 ^{o}C. In the case of procedure-2, this peak appeared at 306.61 ^{o}C. In procedure-3, HNS gave interesting and different results then the others. It gave two exothermic peaks at 292.27 ^{o}C and 341.02 ^{o}C.



Procedure-1



Procedure-2

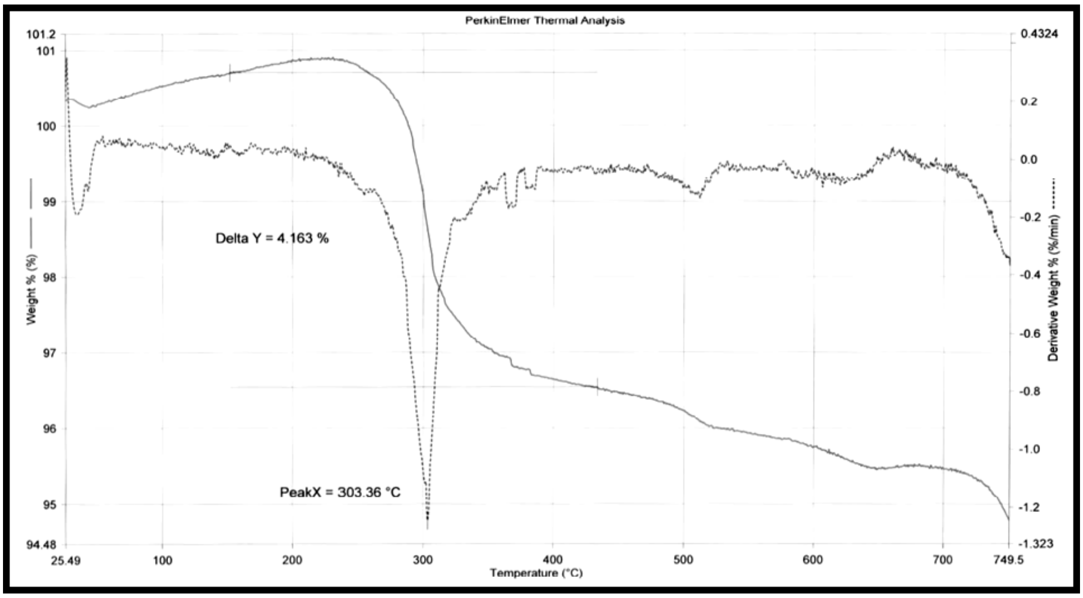


Procedure-3

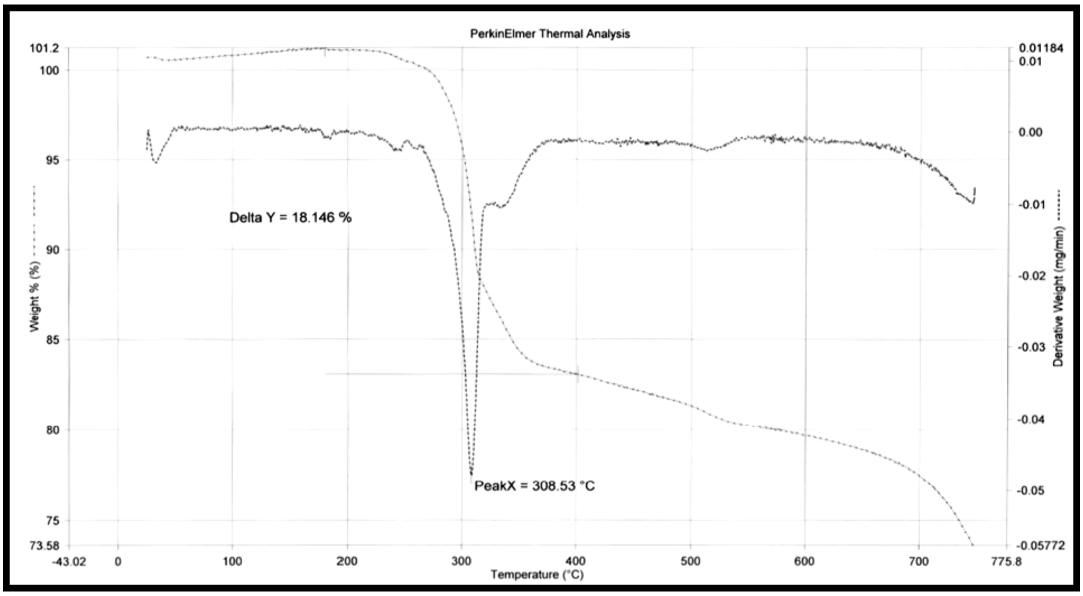
Figure 3.14. The differential scanning calorimetry (DSC) results of HNS for Procedures 1-3.

3.3.2.2. Thermal Gravimetric Analysis

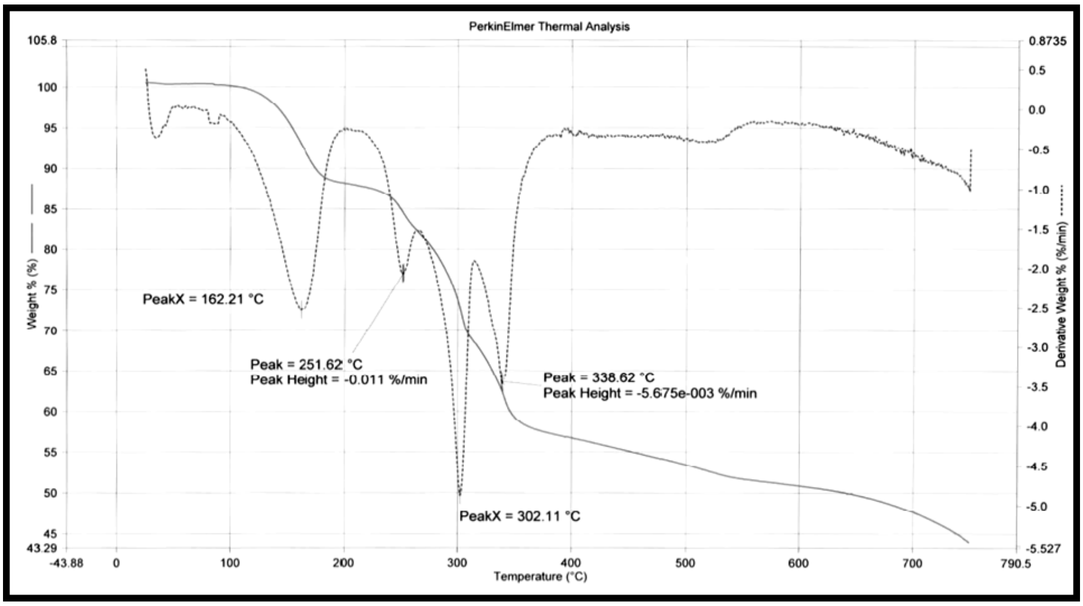
Thermal gravimetric analysis (TGA) determines the loss of mass when a sample is heated or maintained at constant temperature as a function of time [80]. Furthermore, TGA gives information about thermal stability and decomposition [77]. The results of thermogravimetric analysis (TGA) at a heating rate of 10 ^{o}C /minute for a constant sample weight of 5 mg are shown in Figure 3.15.



Procedure-1



Procedure-2



Procedure-3

Figure 3.15. Thermogravimetric Analysis (TGA) result of HNS for Procedures 1-3.

3.3.3. Sensitivity Analysis

A good quality military explosive must be as insensitive as possible. It should not be detonated easily with friction and impact. For this reason, calculating the sensitivity values of HNS gains importance. HNS is known as insensitive explosive. The impact and friction sensitivities of HNS produced by means of procedures 1-3 were measured at TÜBİTAK-SAGE laboratories.

3.3.3.1. Impact sensitivity analysis

The response to a blow is called impact sensitivity. Traditionally, explosives have been subjected to falling weights to measure their impact sensitivities [87]. The results are then reported as the distance for a given weight must fall to produce detonation at 50 percent of the time. In the present study the impact sensitivity test was made by Explosive Research Laboratory (ERL) machine at TÜBİTAK-SAGE. Test results are given in Table 3.1.

Table 3.1. The impact sensitivity test results of HNS obtained for Procedures 1-3.

	Impact Sensitivity (Nm or Joule)	**Explanation**
HNS-Procedure-1	**4.6 J**	1 kg load was released from a height of 90 cm. It was gradually decreasing until 47 cm, at 47 cm the reaction (explosion) was observed. After which, 1 kg load was released from a height of 46 cm for six times and negative results was observed. Finally, shock sensitivity was calculated using the formula $E = mgh$ ($g = 10\ m/sn^2$).

HNS-Procedure-2	**4.6 J**	1 kg load was released from a height of 90 cm. It was gradually decreasing until 47 cm, at 47 cm the reaction (explosion) was observed. After which, 1 kg load was released from a height of 46 cm for six times and negative results was observed. Finally, shock sensitivity was calculated using the formula E = mgh (g = 10 m/sn^2).
HNS-Procedure-3	**6 J**	1 kg load was released from a height of 90 cm. It was gradually decreasing until 61 cm, at 61 cm the reaction (explosion) was observed. After which, 1 kg load was released from a height of 60 cm for six times and negative results was observed. Finally, shock sensitivity was calculated using the formula E = mgh (g = 10 m/sn^2).

According to test results in Table 3.1, HNS produced either by procedures-1 or -2 has impact sensitivity of 4.6 joules. On the other hand, HNS produced by procedure-3 has impact sensitivity of 6 joules. These results imply that HNS from procedures-1 and-2 has the same impact sensitivity and HNS from procedure-3 has lower impact sensitivity. It means that procedure-3 HNS was more insensitive than the other two.

To be insensitive to impact sensitivity value must be between 3.5-8 joules [88]. Therefore, all HNS samples are insensitive to impact.

3.3.3.2. Friction Sensitivity Analysis

Friction sensitivity tests are made to determine the relative safety of an explosive during processing. The test results are given in Table 3.2. The maximum value (360 N) was applied to all three HNS sample for six times. Even at this maximum value, no reaction took place. Therefore, the friction sensitivity of three samples was reported as 360 N. According to the literature, HNS has friction sensitivity value as 240 N [88]. It means that all three HNS samples have much more insensitivity to fricton than the literature suggests.

Table 3.2. The friction sensitivity test results of HNS obtained for Procedures 1-3.

	Friction Sensitivity (N)	**Explanations**
HNS-Procedure-1	**360 N**	Material to be tested was placed on the ceramic platform just above the red buton. After that, porcelain pin was placed on the material. Different weights were mounted on lever, then with the help of engine friction was done. The highest value that device could apply was 360 N. At this value, material did not give reaction for six times. Therefore, a sensitivity value of friction was reported as 360 N.
HNS Procedure -2	**360 N**	
HNS-Procedure -3	**360 N**	

3.4. HNS SYNTHESIS WITH TRANSITION METAL OXIDATION (BELLAMY PROCEDURE)

Hexanitrostilbene was also synthesized with transition metal oxidation with the help of mild base sodium benzoate [75]. In addition to the Shipp procedure, also this method was tested for HNS synthesis. According to this method, trinitrotoluene was dissolved in dimethylsulfoxide (DMSO). After that sodium benzoate and anhydrous copper (II) chloride ($CuCl_2$) were added. After heating at 50 ^oC for 10 h HNS was produced. Although high yield was obtained, the procedure involves lots of diffuculties to apply this procedure to industry. The first problem arose from the solvent. Dimethyl sulfoxide is an expensive solvent. Therefore, it should be recycled after reaction. However, dimethyl sulfoxide (DMSO) could not be recycled after reaction because of its decomposition. In addition, it could not be entirely removed from the product which decreases the thermal stability. Secondly, similar problems come from the oxidant copper (II) chloride ($CuCl_2$). It was used nearly one to one ratio with TNT. According to experiments for 1000 g TNT, 900 g anhydrous copper (II) chloride ($CuCl_2$) has to be used. It could not be recycled like solvent. As a result, HNS production from this method is not feasible for industry. The experiments were carried out to this procedure. The yield (58 %) was lower than the literature yield (82 %). The Nuclear magnetic resonance (NMR) results were given in Figure. 3.16. The olefinic peak occured at δ 7.2 and phenyl peaks resonate at δ 9.15

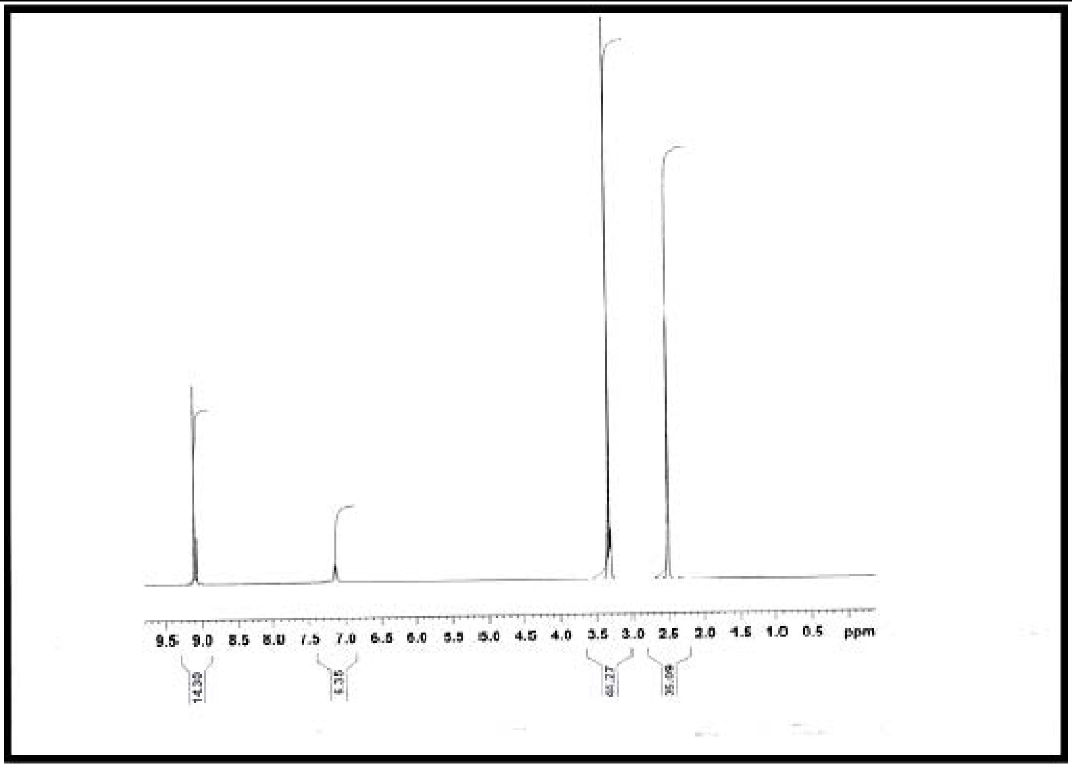


Figure 3.16. ^{1}H-NMR spectrum of HNS obtained from Bellamy Process (Procedure-4).

The Fourier Transform Infrared Resonance Spectroscopy (FTIR) results also was taken. The results are given in Figure 3.17.

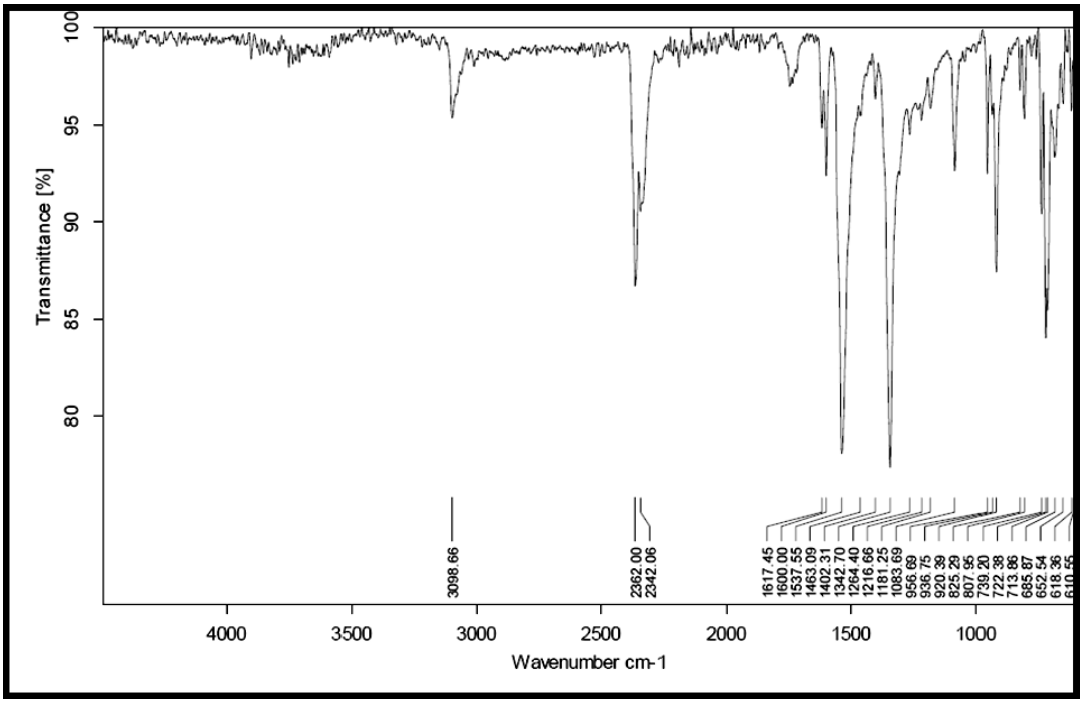


Figure 3.17. The Fourier Transform Infrared Resonance Spectroscopy (FTIR) of HNS obtained from Bellamy Process (Procedure-4).

CHAPTER 4

CONCLUSION

In this study, the synthesis of hexanitrostilbene (HNS) was realized by means of the Shipp and Bellamy processes. Firstly, experiments were made on the basis of the Shipp process, because of the applicability of this process to industrial scale. Initially unknown points of the process (reaction temperature, solvent amount, reaction time, reaction pH and NaClO addition) were evaluated. Procedure-1 was developed on the basis of this information. After that, the works were done to solve the problems arising within this procedure. These were low yield, safety, high solvent amount and purification. Procedure-2 and procedure-3 were developed to solve these problems of procedure-1. They are the modified versions of the Shipp process. After all, the optimizations were done for the reaction temperature, solvent amount, NaClO amount and reaction time. The results are shown at Table 4.1.

Table 4.1. The optimization results for Procedures 1-3. A: Solvent Type, B: Solvent Amount, C: Co-solvent Type, D: Co-solvent Amount, E: TNT Amount, F: Sodium Hypochloride Amount, G: Reaction Temperature, H: Mixing Time, I: Yield in Grams, J: Percent Yield.

Procedure	A	B	C	D	E	F	G	H	I	J
1	THF	9 ml	Methanol	12.5 ml	1.5 g	10 ml	5 °C	150 min.	0.57 g	38 %
2	Dioxane	5 ml	Methanol	12.5 ml	1.5 g	11 ml	20 °C	120 min.	0.82 g	54 %
3	Dioxalane	6 ml	Methanol	12.5 ml	1.5 g	10 ml	15 °C	80 min.	0.73 g	49 %

Procedure-1 was highly affected by temperature changes. The highest yield was gotten at 5 ^{o}C and reaction should be carried in a cold medium. Also among the procedures, the highest amount of solvent was used in this procedure. The solvent (Tetrahydrofuran (THF)) amount was 9 ml for 1.5 g of TNT. In addition, the yield (38 %) was lower than other procedures. In procedure-2, dioxane was used instead of THF. The effect of temperature was less than the others. This procedure was carried out 20 ^{o}C. Another important result was possibility of decreasing the solvent amount. Only 5 ml solvent was used for 1.5 g of TNT. Furthermore, the highest yield (54 %) was observed in this procedure. Procedure-3 gave similar results to procedure-2. The solvent amount was 6 ml for 1.5 g of TNT. The reaction temperature was 15 ^{o}C. Resulting yield was 49 % for procedure-3.

THF involves peroxide, and this could cause explosion during reaction. However, this was prevented by using dioxane and dioxalane at procedure-2 and procedure-3. All three procedures were exothermic and sudden increase of temperature was observed. This sudden increase could cause fire accident at THF medium. The lower flammability of dioxane and dioxalane prevents fire accident probability. As a result, procedure-2 and procedure-3 are much safer than procedure-1.

The raw products of all the procedures involved lots of impurities. To remove these impurities and increase the bulk density, crystallization was applied to raw materials. Applying two successive crystallization procedures to the raw materials eliminated impurities and increased the bulk density.

Also, HNS synthesis was done on the basis of the Bellamy process. Although, the highest yield (58 %) of HNS was obtained, this procedure involves some problems. The high cost of solvent (dimethylsulfoxide (DMSO)) and oxidant ($CuCl_2$) and impossibility of recycling of those materials prevent this procedure to be applied for large scale production.

At the end of study, the analyses of resulting HNS samples were done. Spectroscopic analysis (NMR, FTIR) showed that high purity HNS was produced for the first two procedures (Procedure-1 and Procedure-2). A small amount of hexanitrobibenzyl (HNBB) formation was observed at Procedure-3. The most important property of HNS is the thermal stability. According to DSC and TGA results, HNS produced by all the procedures exhibited high thermal stability and the samples decompose above 300 ^{o}C. In addition to these analyses, the sensitivity analysis was done. The impact sensitivity results showed that HNS of procedure-1 and procedur-2 have the same impact sensitivity. Moreover, impact sensitivity of procedure-3 was lower than the other two. This means that HNS from procedure-3 was more resistant to impact than other two HNS sample.The reason could be the HNBB formation at this procedure. In addition, friction sensitivity test was performed. The maximum value (360 N) was applied to all three HNS samples. Even at this maximum value, no reaction took place. As a result, all HNS samples have high resistance to impact and friction and this makes them safe.

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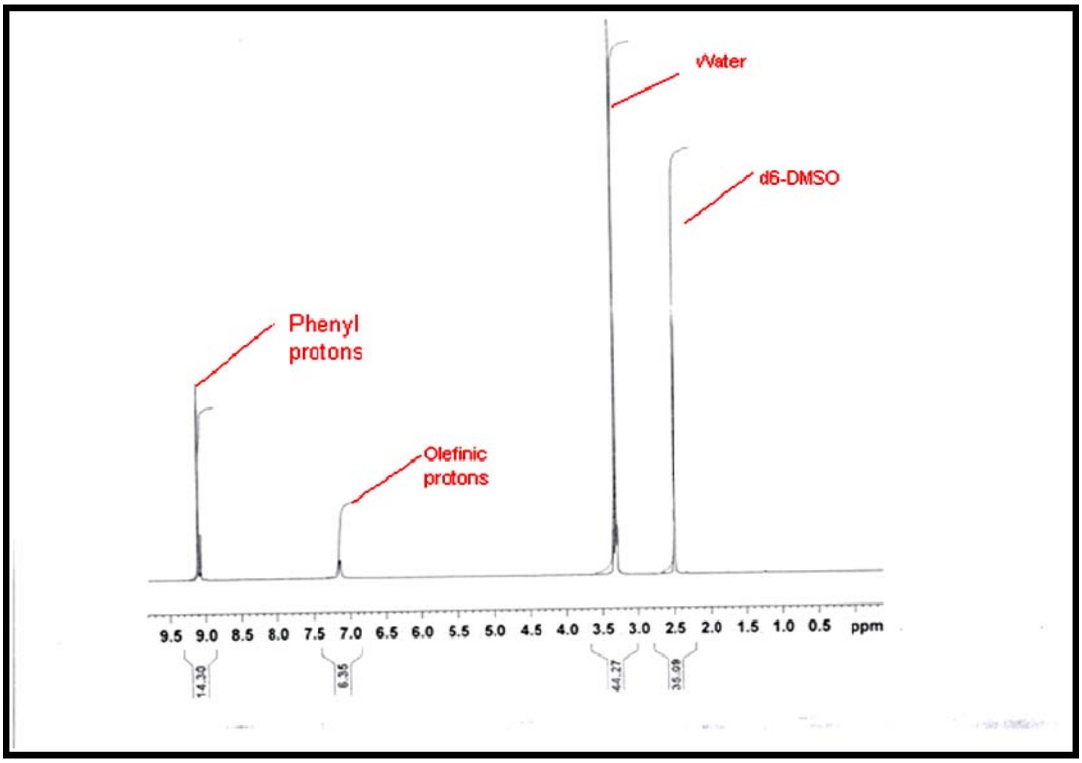
APPENDIX A

NMR DATA

NMR spectra were recorded on a Bruker DPX 400.

Chemical shifts δ are reported in ppm relative to **d_6**-DMSO (^{1}H: δ=2.5), **d_6**-DMSO (^{13}C: δ=40.0) and) as internal standards.

^{1}H and ^{13}C NMR spectra of products are given below.



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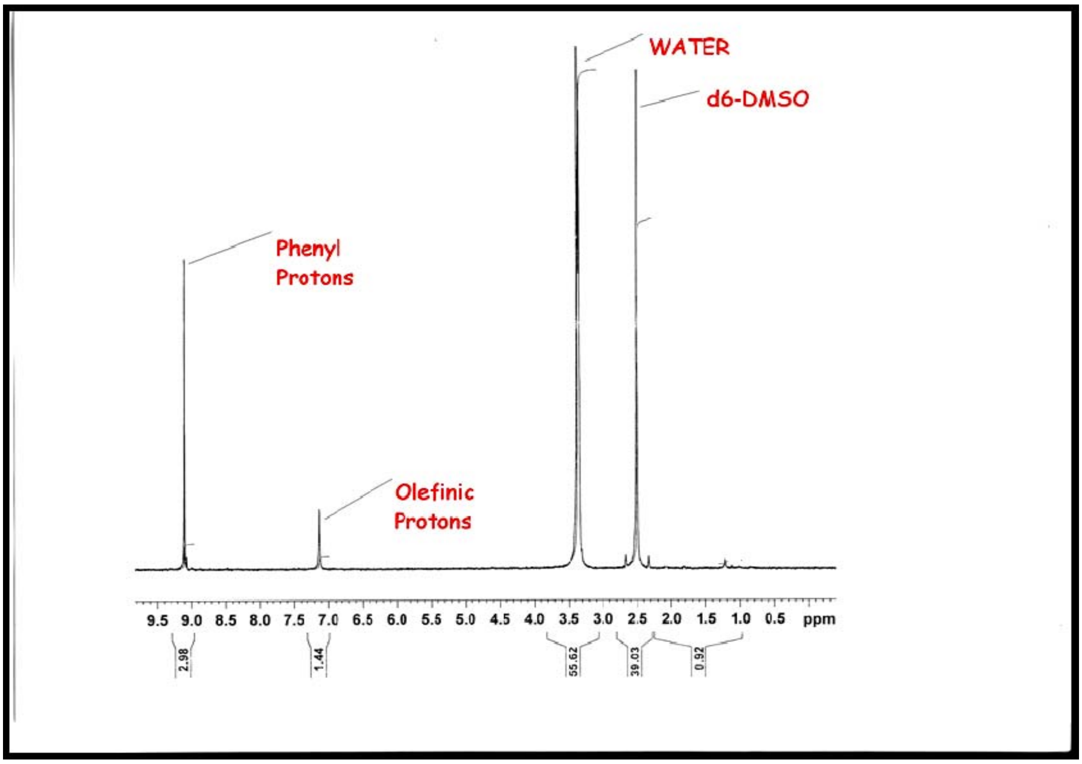
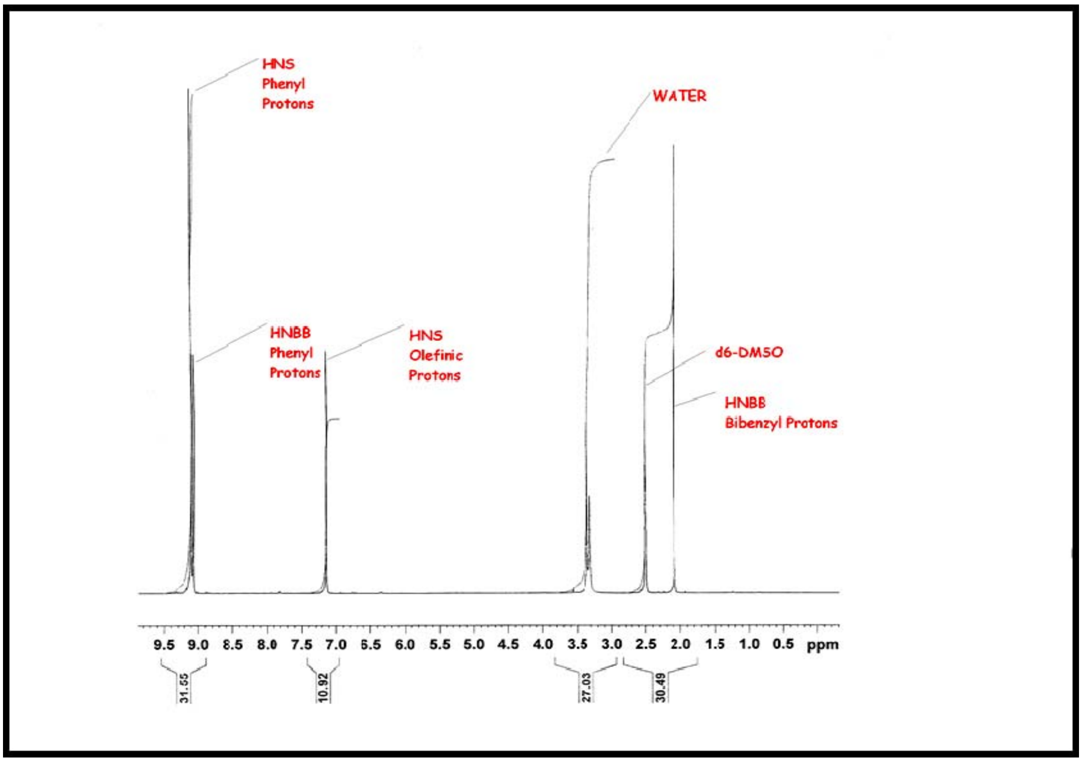
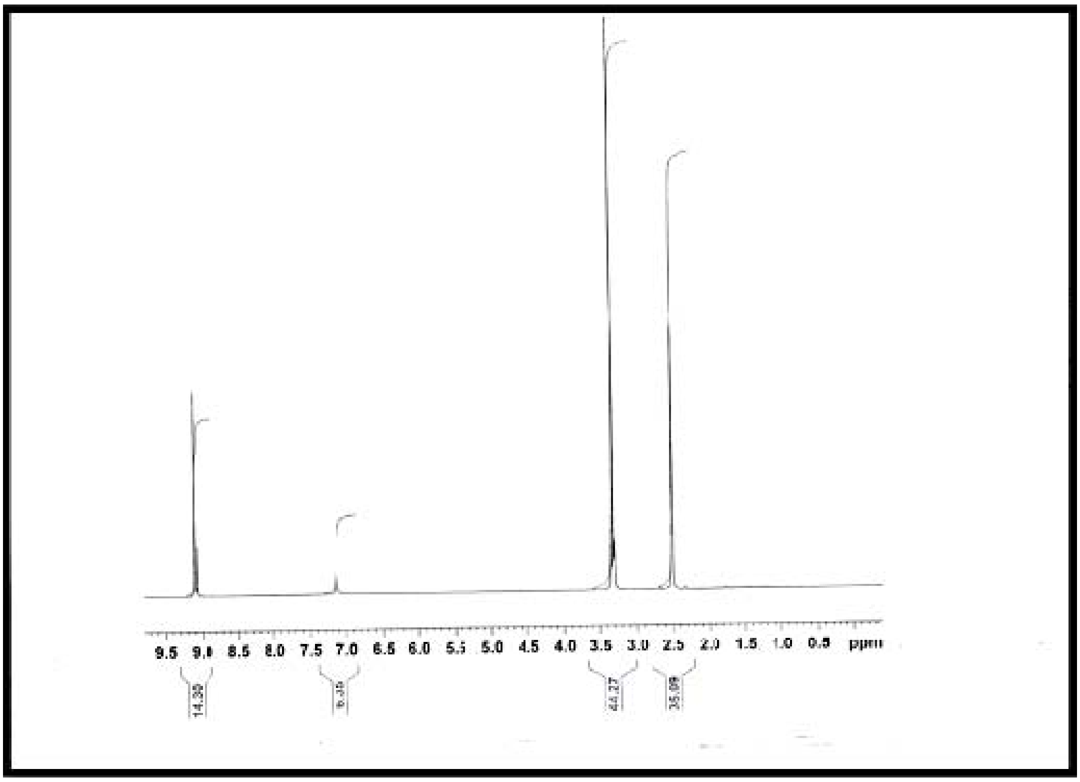


Procedure-2

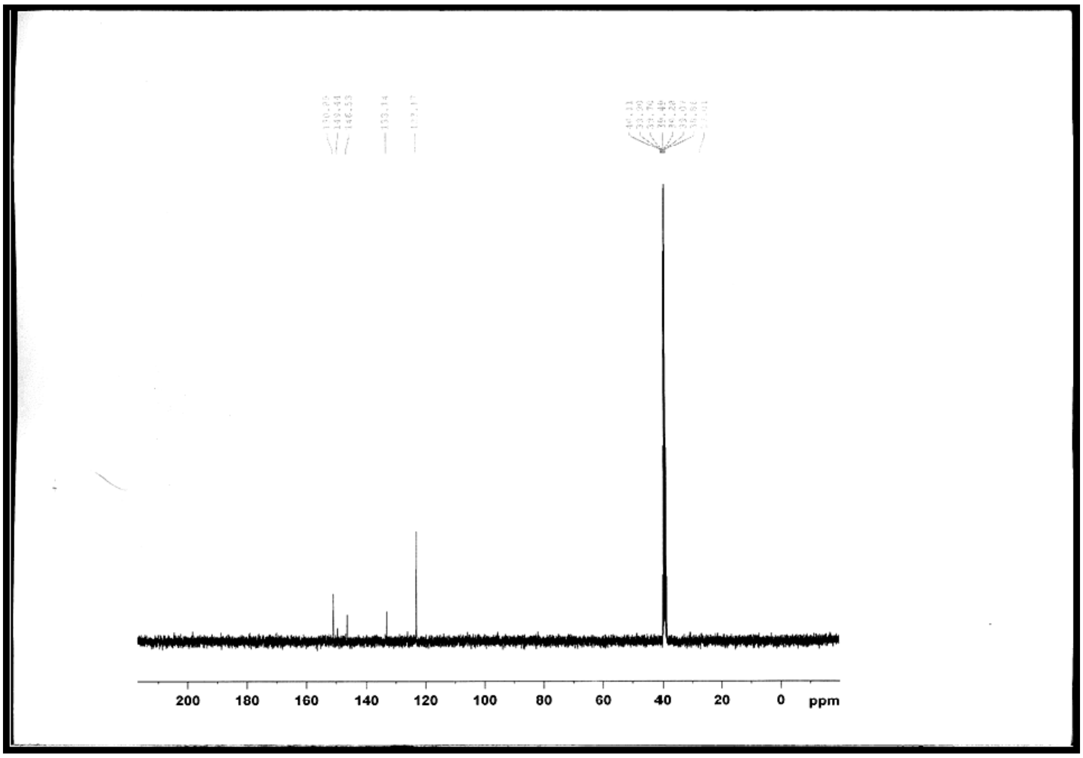


Procedure-3

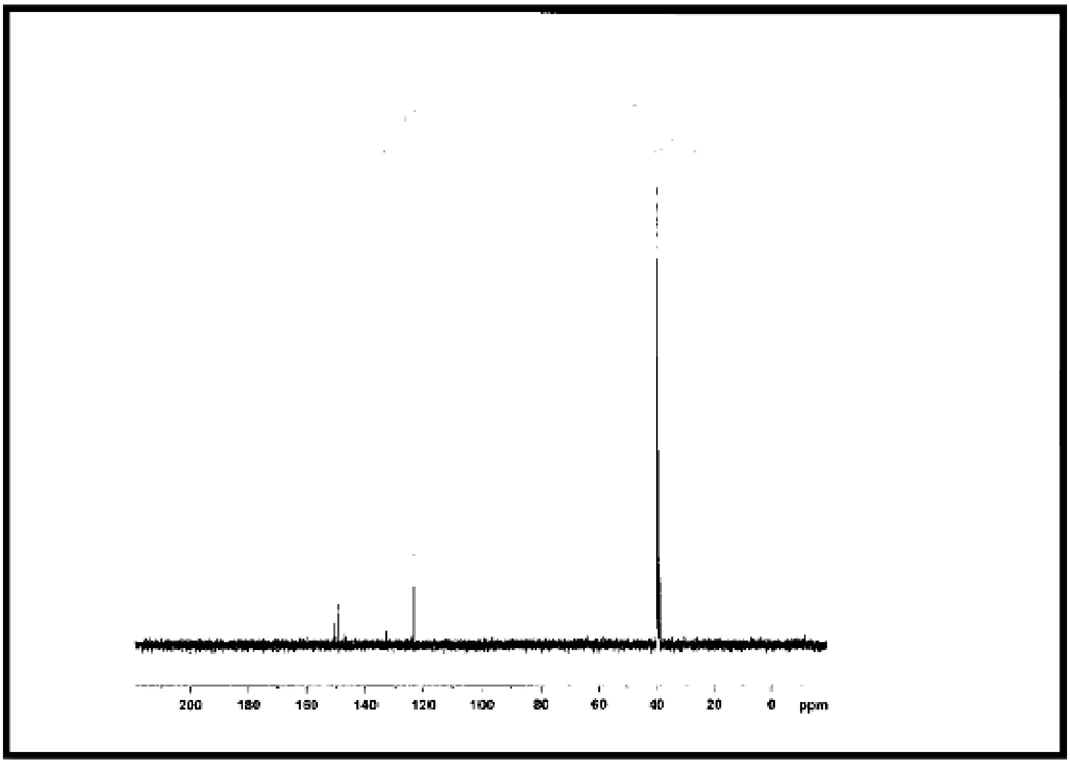


Procedure-4

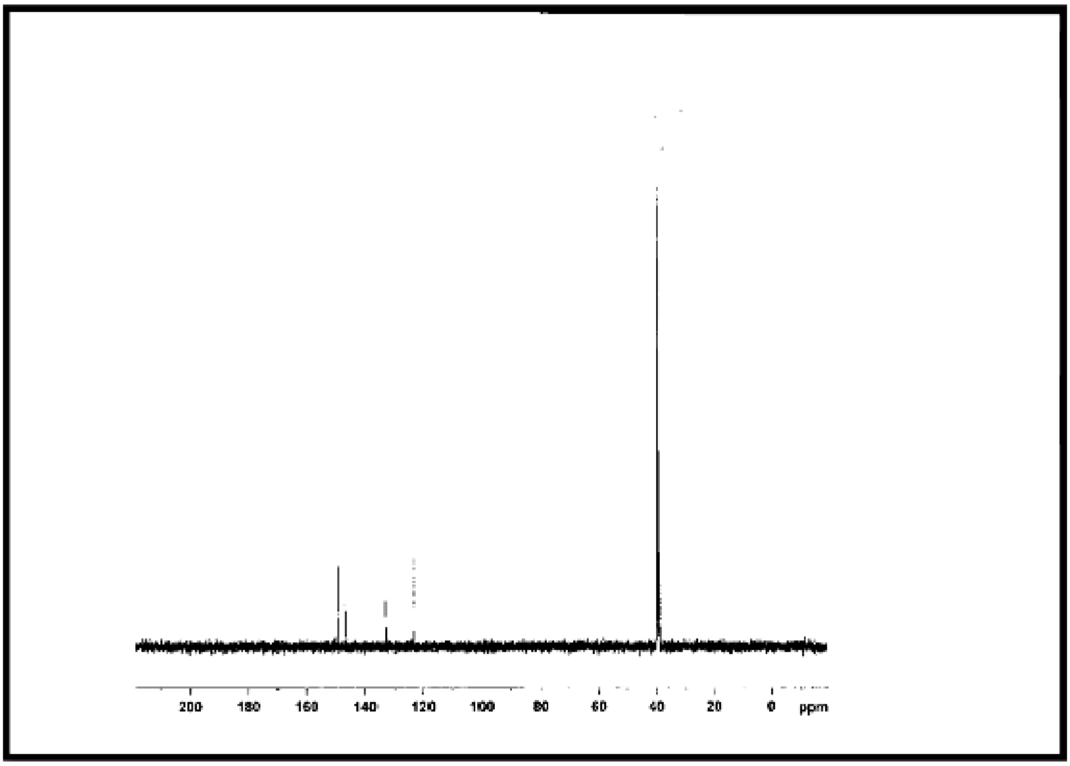
Figure A.1. ^{1}H-NMR spectra of Procedures 1-4.


150.25
149.44
146.53
133.14
123.17
40.11
39.90
39.70
39.49
39.28
39.07
38.86
200
180
160
140
120
100
80
60
40
20
0
ppm

Procedure-1



Procedure-2



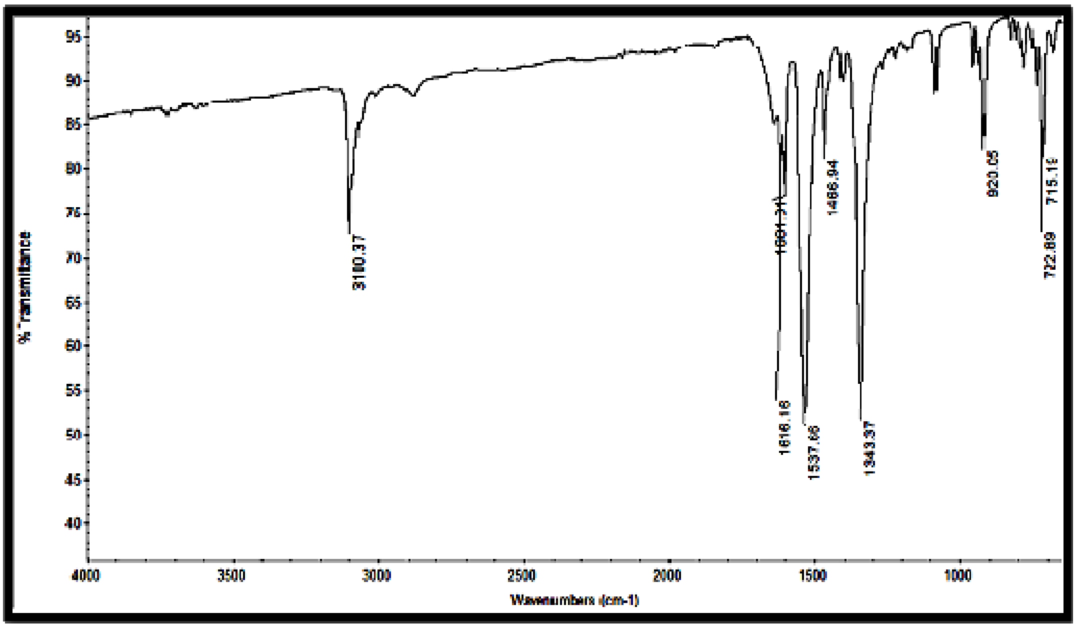
Procedure-3

Figure A.2. ^{13}C-NMR spectra of Procedures 1-3.

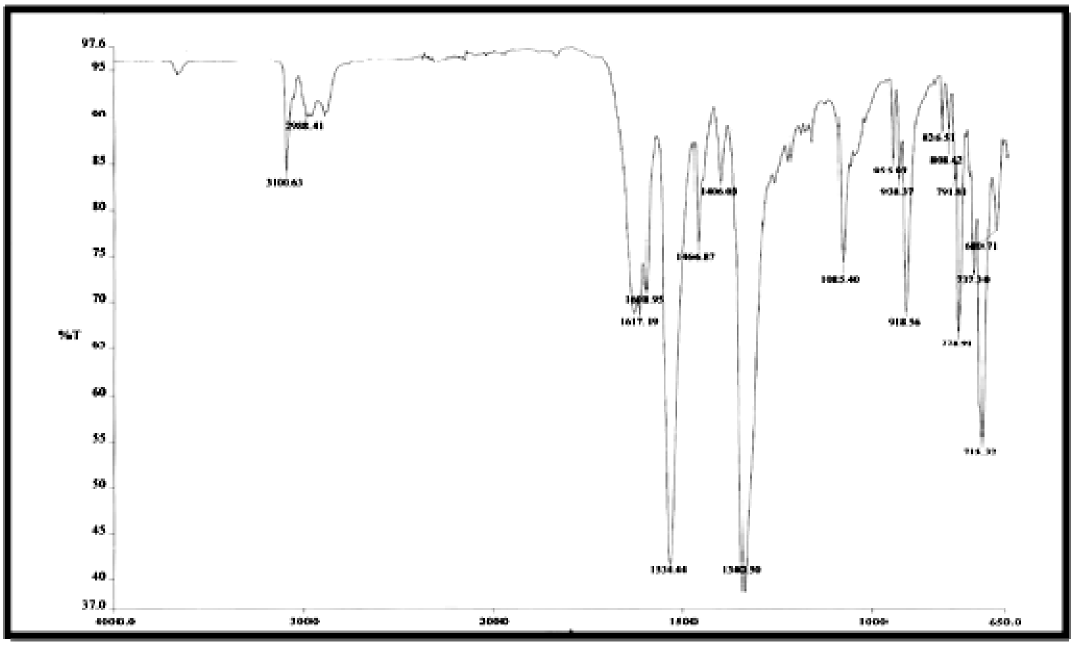
APPENDIX B

FOURIER TRANSFORM INFRARED RESONANCE SPECTROSCOPY (FTIR) DATA

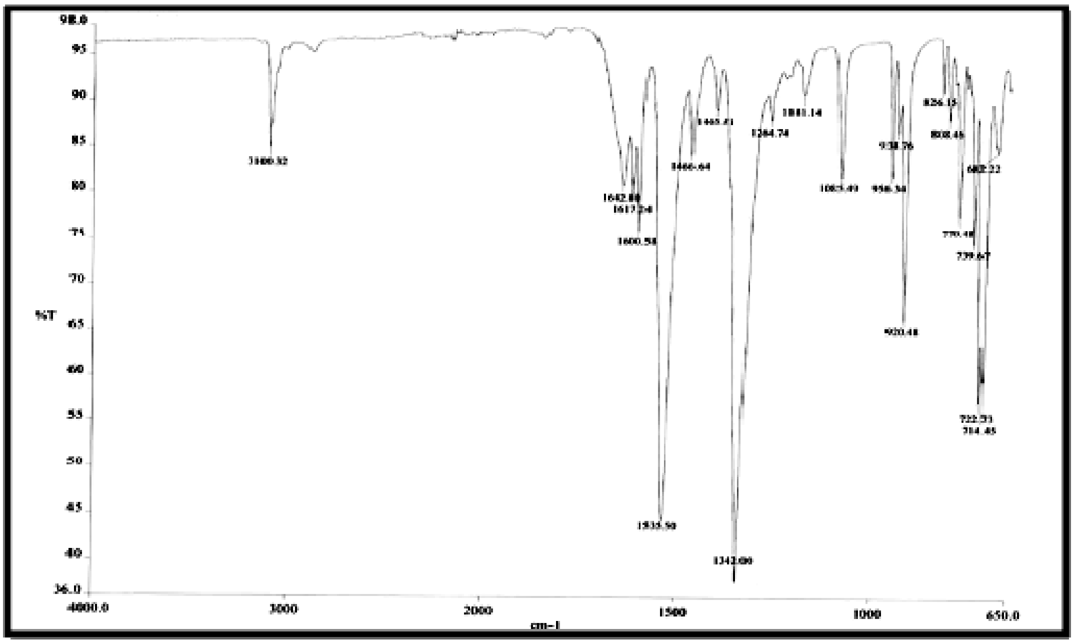
FTIR spectra were taken by Perkin Elmer Spectrum 100 FTIR spectrometer.



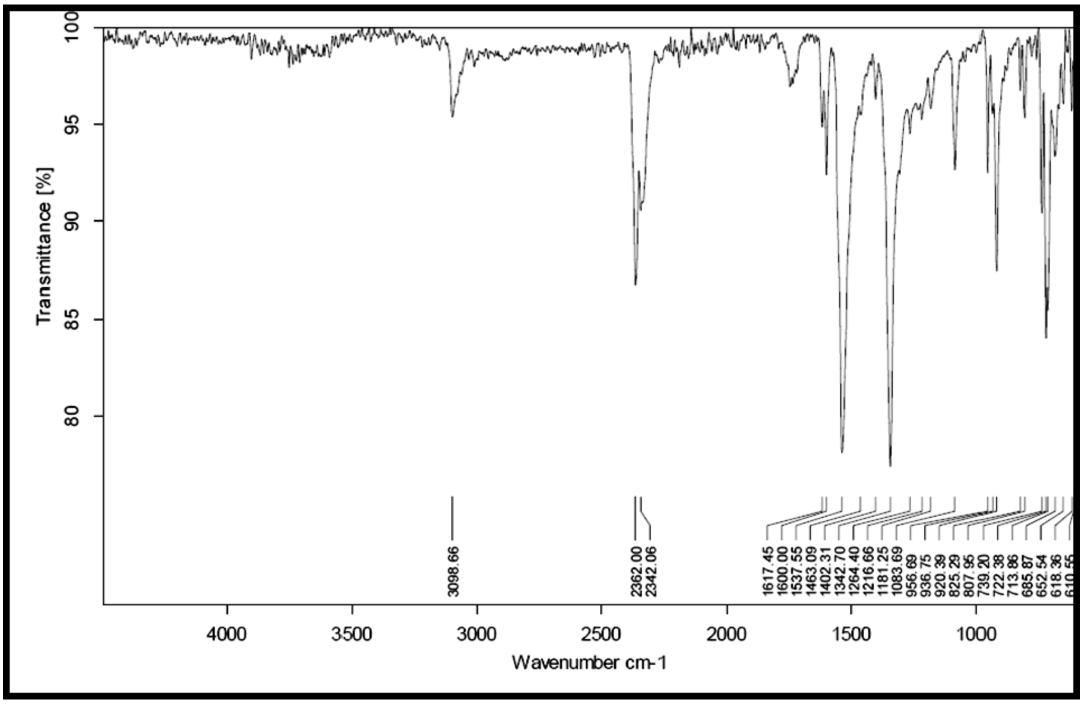
Procedure-1



Procedure-2



Procedure-3



Procedure-4

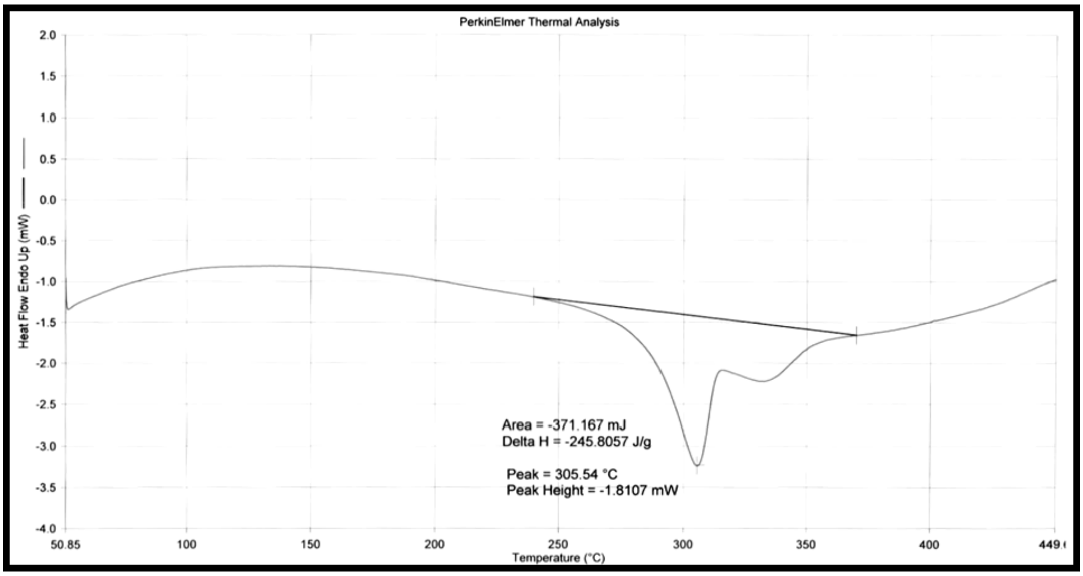
Figure B.1. FTIR spectra of HNS for Procedures 1-4.

APPENDIX C

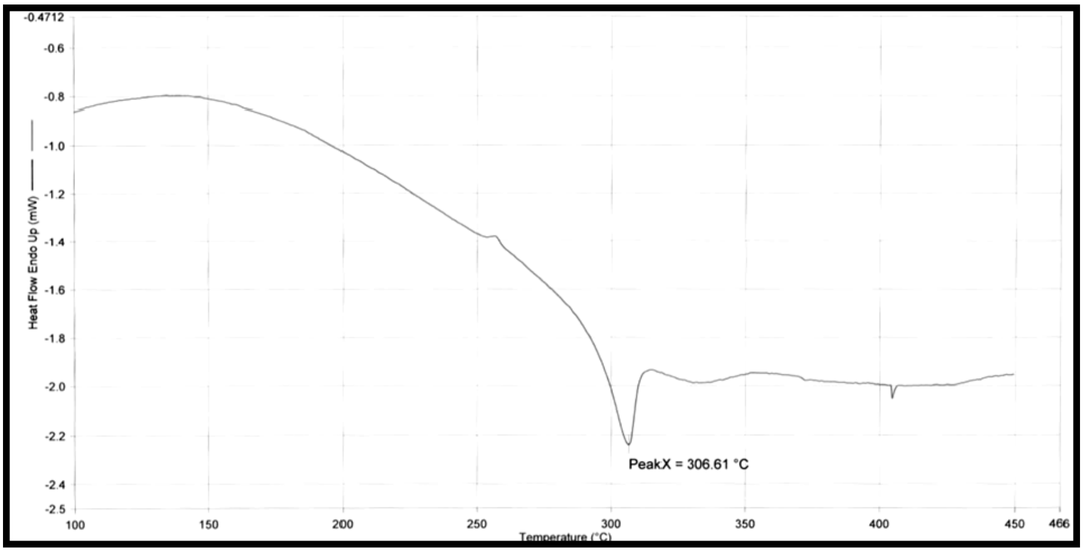
DSC RESULTS

DSC results were recorded on Perkin Elmer Diamond DSC

DSC results are given below.



Procedure-1



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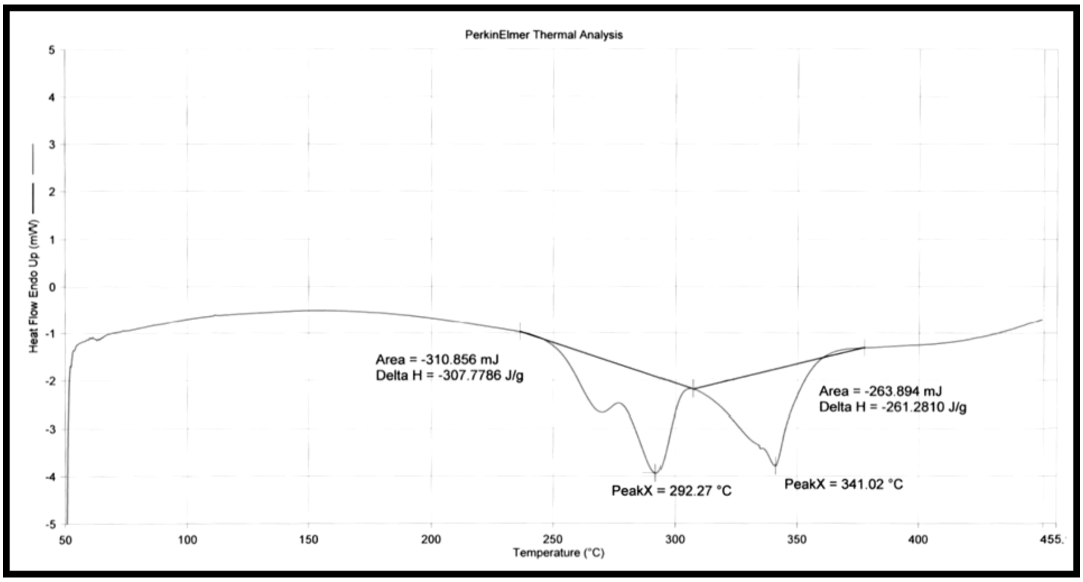


Procedure-3

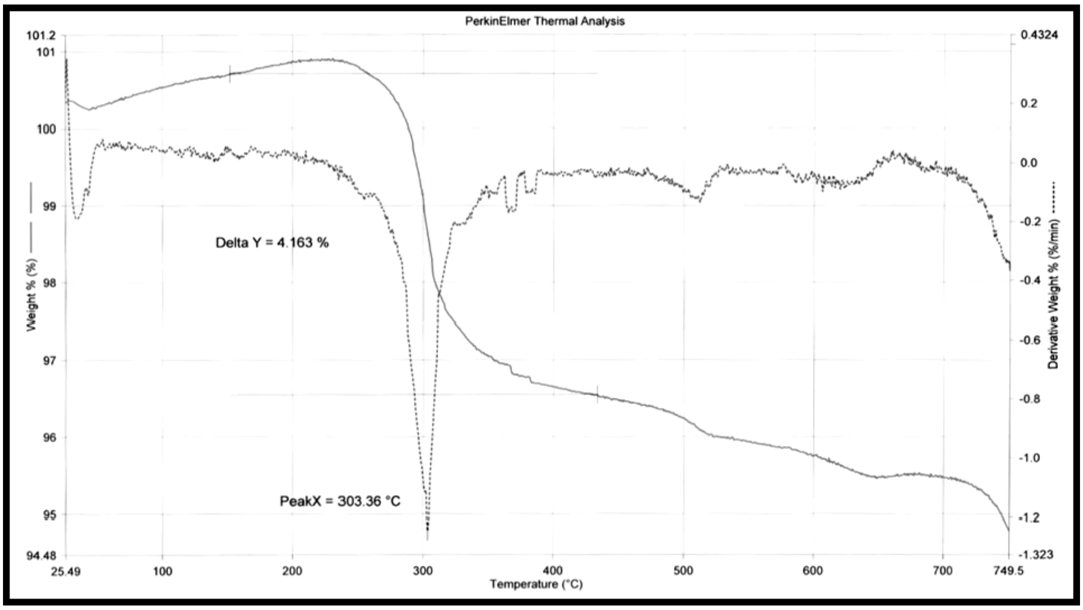
Figure C.1. The differential scanning calorimetry (DSC) results of HNS for Procedures 1-3.

APPENDIX D

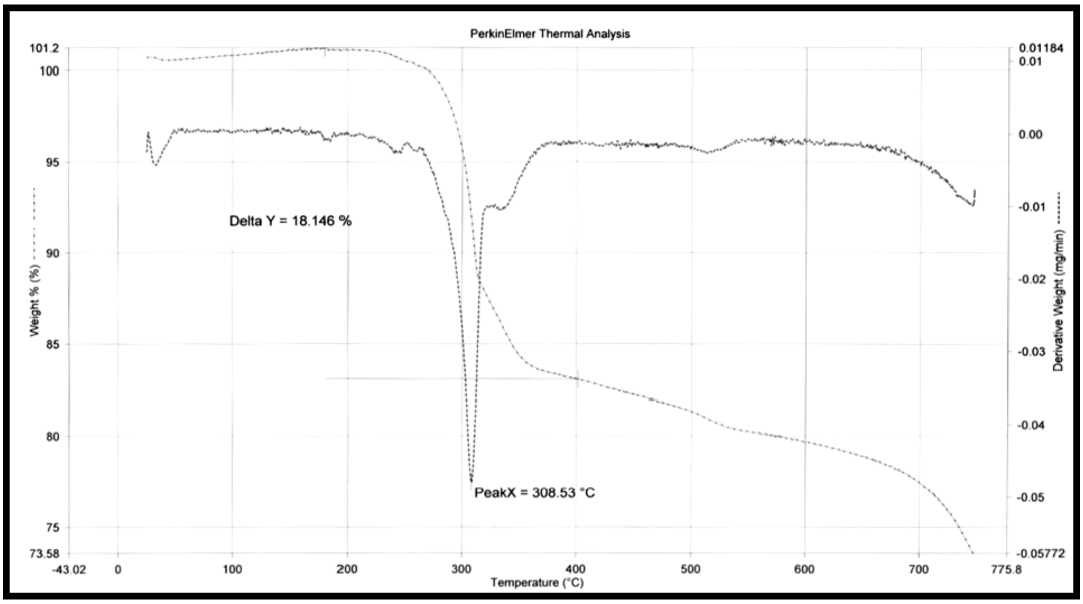
TGA DATA

TGA results were recorded on Perkin Elmer Pyris

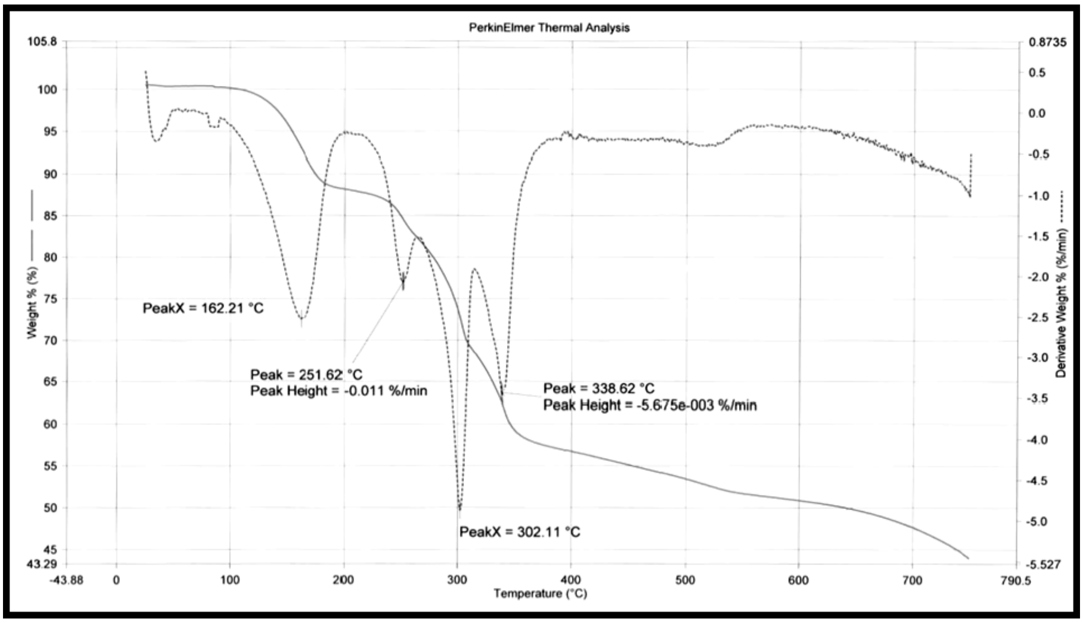
TGA results are given below.



Procedure-1



Procedure-2



Procedure-3

Figure D.1. Thermogravimetric Analysis (TGA) results of HNS for Procedures 1-3.